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CHEMILUMINESCENT OZONE MEASUREMENT PROGRAM-- OZONE TOTAL OXIDANT RELATIONSHIP IN AMBIENT AIR

by

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Research Triangle Park,
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Prepared for

National Air Pollution Control Administration
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FOREWARD

This report was prepared by members of the Engineering and Environmental Sciences Division of the Research Triangle Institute, Research Triangle Park, North Carolina under Contract No. PH 22-68-30.

The work on the project was initiated by the National Air Surveillance Network Section, Air Quality and Emission Data Program, National Air Pollution Control Administration and was under the direction of Mr. E. C. Tabor.

The work was performed by the Engineering and Environmental Sciences Division under the general supervision of Dr. R. M. Burger, Director. The Project Director was Mr. James R. Smith and the Principal Scientists were Dr. H. G. Richter and Dr. Lyman A. Ripperton. Mr. Cliff E. Decker performed calibration experiments for RTI. Mr. Raymond Garriss was responsible for equipment maintenance and field measurements. Computer programming support was provided by Mr. Richard C. Haws and Mrs. Christina M. Davis.

The Research Triangle Institute wants especially to acknowledge the cooperation and assistance provided throughout the experimental phase of the program by Mr. Frank McElroy of the National Air Pollution Control Administration who has overall responsibility for the performance of CAMP Station instruments, by Mr. Allen Trackenburg, principal operator of the Philadelphia Station, and by Mr. William Lamar of the Denver Station. Mr. Robert Lee, Mr. Charles Scow, and Mr. Raymond Lozano represented the National Air Pollution Control Administration and participated in the several calibration experiments at the two Stations.

ABSTRACT

Ozone and total oxidant in ambient air were measured simultaneously for a two month period in Philadelphia and a similar period in Denver, Colorado. Ozone was measured by the chemiluminescent technique and total oxidant by both colorimetric and coulometric techniques. The ozone and total oxidant instruments were calibrated by a constant ozone source (standardized by the neutral KI analytical technique) at the beginning and end of each experimental period.

The chemiluminescent instrument operated satisfactorily more than 97% of the time, but the colorimetric total oxidant instruments operated satisfactorily less than 50% of the time.

Except for times of rain or heavy cloud cover, ozone concentrations, as measured by the chemiluminescent technique, exceeded total oxidant levels, as measured by the colorimetric KI technique, during daylight hours in Philadelphia. The same anomalous results were obtained in Denver during a period of time when the CAMP Station oxidant instrument was sampling from the station manifold. During a period of time when the colorimetric and chemiluminescent instruments were sampling from a special manifold, total oxidant concentration usually exceeded the ozone concentration.

The ratio of ozone to total oxidant concentration in Philadelphia varied from 0.17 to 1.9 while in Denver it varied from 0.50 to 1.6 It is thus not possible to calculate ozone concentrations in urban air from measured total oxidant concentrations with any degree of confidence.

The oxidant and ozone maxima occurred 2 hours earlier in Denver than in Philadelphia.

On numerous occasions an increase in ozone and/or total oxidant concentrations were noted during hours of darkness.

On numerous occasions more than 4 pphm of ozone were found to co-exist with 4 pphm of NO.

The data obtained during this program indicate that the chemiluminescent ozone measurement is more specific and less subject to interference than the colorimetric or coulometric "total oxidant" measurement and would, therefore furnish a more reliable index of air quality.

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SECTION I

INTRODUCTION

Inherent in the concept of air quality is a knowledge of the concentration and behavior of those constituents used as a measure of air quality. Important among these are ozone and total oxidant. The primary objective of the study reported upon herein was to examine the quantitative relationship between ozone and total oxidant concentrations in the urban areas of Philadelphia, Pennsylvania, and Denver, Colorado. A specific objective was to determine the degree to which total oxidant measurements obtained from the standard CAMP Station colorimetric total oxidant meter could be interpreted as a measure of ozone concentration.

A similar, but brief, study was conducted at Cincinnati, Ohio; Washington, D. C.; Denver, Colorado; and Los Angeles, California in 1967.[1] Data were obtained over a two week period at each location. The limited number of observations obtained were not sufficient to establish a meaningful relationship between ozone and total oxidant. The data did, however, emphasize the complexity of the problem and the need for a more precise experiment covering a longer period of record. The second study, reported upon here, began June 1,1968 for two (2) months in each of two cities, Philadelphia and Denver.

SECTION II

MEASUREMENT TECHNIQUES

Crucial to an understanding of the data obtained in this later study is an understanding of the instrumentation used to acquire it. The chemiluminescent technique for ozone measurement was developed by Regener.[2] The principle on which the instrument operates is one in which ozone reacts with certain organic compounds causing the emission of a minute amount of light. The amount of light, when viewed by a photomultiplier tube, is proportional to the ozone concentration. The current output from the photomultiplier can be displayed on a strip chart recorder and a permanent record of the ozone concentration obtained. The chemiluminescent ozone meter used in this present study has an integral dynamic calibration system so that the strip chart actually shows alternate signals from ambient ozone levels and the calibration system in a ten minute cycle. In addition, the chemiluminescent meter provides for a record of the electronic stability of the system as well as that of the recorder.

No compound yet found in polluted air, at usually experienced concentrations, is known to cause a false signal in the chemiluminescent meter.[3] Sulfur dioxide in high concentrations (0.5 ppm and above) is reported[4] to cause some decrease in response for a given ozone concentration, but details of the interference are not known beyond the fact that prolonged exposure of the sensitive element to the SO_2 is required. In summary, the chemiluminescent technique for ozone measurement is extremely sensitive and thought to be specific for ozone.

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As embodied in the Regener instrument, the technique permits extended monitoring of ozone in polluted air with concurrent calibration signals for accurate comparison of the data from beginning to end of an experimental period.

The standard CAMP Station total oxidant instrument used in this study operates on a colorimetric principle. In this instrument, oxidant in the sampled air reacts with a neutral buffered solution of KI, oxidizing the iodide to iodine. The quantity of iodine released, as measured by a photometer, is proportional to the oxidizing ability of the air expressed as ppm ozone. A signal from the photometer is displayed on a strip chart for permanent record. Periodically, the sample air is stopped and the optical density of the unreacted solution is sensed by the photometer, and the instrument is automatically "zeroed" to correct for baseline drift. After this operation, the instrument is again ready for oxidant measurements above a "zero-background".

The neutral buffered KI technique, as an analytical method for ozone, suffers from a number of known interferences. Any species capable of oxidizing iodide to iodine can, in principle, be measured by this technique, thus providing a positive interference in the ozone measurement. In practice, because of kinetic considerations, many of the oxidizing agents in the atmosphere are incompletely reduced by the iodide in the time it takes the sample to reach the photometer. The fraction of the oxidizing agent so reacted depends upon many factors--with the result that the iodine passing through the photometer comes from the ozone reaction (very rapid) plus other unknown oxidizing agents of unknown concentration reacting to an unknown extent.

The second kind of interference experienced by the total oxidant meter results from SO_2, and possibly other unknown reducing agents. For example, iodine formed by ozone in the neutral buffered KI solution, is reduced rapidly to iodide by SO_2. The reaction is stoichiometric, with the result that one molecule of SO_2 "prevents" one molecule of ozone from being observed. Other reducing agents in the atmosphere will behave similarly, but, because the nature and concentrations of other reductants are unknown, their possible interference with the KI instruments is quantitatively unknown.

One procedure for eliminating this interference is to pass the incoming air stream through a CrO_3 "scrubber" whereupon the SO_2 is oxidized to SO_3, which does not react with iodine. At the same time, however, some of the NO in the air stream is oxidized to NO_2 which is capable of oxidizing iodide to iodine. Thus, in eliminating a "negative" interference, a "positive" interference has been introduced. The NO (via NO_2) contribution to observed total oxidant concentrations is usually taken to be 11% of the concurrent NO concentration[5] and is so corrected in these studies. In most polluted urban atmospheres, it is expedient to use the CrO_3 scrubber because the SO_2 concentrations are frequently high whereas during periods when ozone exists, NO is usually in low concentration. The scrubber has been shown[6] to pass ozone quantitatively.

In summary, the total oxidant instruments used in the CAMP Stations are, in the absence of interfering substances, capable of measuring ozone efficiently, and other oxidizing agents inefficiently. A CrO_3 scrubber eliminates negative interference from SO_2 (and possibly other

reducing agents) but creates positive interference from NO. This latter must be monitored concurrently and its effect subtracted from total oxidant readings.

A third instrument was also used during the experimental program, a coulometric total oxidant meter.[9] It also operates on the principle that oxidants in the sampled air oxidize iodide ion (in a neutral buffered KI solution) to iodine. The iodine so formed passes over an electrode and upsets an equilibrium which has been established. The current required to re-establish this equilibrium is a measure of the oxidants concentration in the air. This technique suffers from the same interferences as the colorimetric technique, both positive and negative. A CrO_3 scrubber was also placed in the intake line to eliminate the reductant interferences.

SECTION III

RESEARCH OBJECTIVES

The objective of this research was to obtain a quantitative comparison between ozone data obtained by the chemiluminescent ozone instrument and total oxidant data obtained by the colorimetric and coulometric total oxidant instruments during a period of two months in each of two cities.

The principal reason for this comparison was to determine whether a correction factor could be applied to the oxidant values to obtain ozone concentrations.

The data were obtained in Philadelphia, Pa. and Denver, Colorado.

SECTION IV

CALIBRATION PROCEDURES

The oxidant instruments used during the measurement program were simultaneously calibrated by having each instrument sample from a manifold through which flowed clean air containing ozone. The neutral buffered KI technique was used as the standard or referee method for measuring ozone concentrations in the manifold air stream. During the first calibration at Philadelphia a portion of the air was sampled from both the inlet and outlet of the manifold and passed through the KI solutions. In this way it was demonstrated that the ozone concentration remained constant in all parts of the manifold during the calibration experiments. Only one KI measurement was made at a time in subsequent calibrations. Calibrations were performed at the beginning and end of the sampling period in each city. The same calibration equipment was used during all tests. In all calibration experiments the station oxidant meter and one coulometric oxidant meter were equipped with fresh CrO_3 scrubbers. The procedures employed are detailed below.

A. Apparatus

(1) Absorbers - All glass midget impingers with ball and socket joints.

(2) Air-metering device - A critical orifice capable of delivering 1 ℓ/min at 20 in. Hg vacuum. Calibrated by wet test meter.

(3) Vacuum source - Gast pump or its equivalent.

(4) Spectronic 20 spectrophotometer.

(5) Manifold - Glass manifold, 1" O. D. pyrex glass, 2 feet long with sampling ports.

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(6) Clean air supply - Cylinder air, passed through charcoal, capable of delivering a minimum of 10 liters per minute through the manifold.

(7) Ozone generator - UV lamp.

B. Reagents

Neutral, buffered KI, 1%. Procedure as specified in the "Selected Methods for Measurement of Air Pollutants".[7]

C. Design of Calibration System

The manifold was set up in such a manner (Fig. 1) as to have a minimum flow of about 10 ℓ/min. The positions in Fig. 1 labeled Chem. #1, #2, and #3, refer to the three sampling lines of the chemiluminescent instrument. Line #3 was placed at the end of the manifold because during a certain portion of the chemiluminescent meter 10-minute cycle, ozone is ejected from this line. In this end position the ejected ozone did not affect the other instruments.

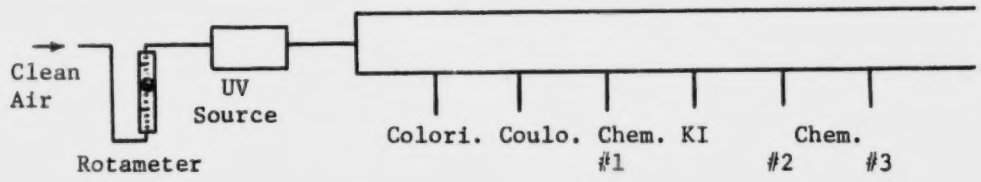

Figure 1. Diagram of Calibration Train and Manifold

The sampling train (Fig. 2) for the KI method consisted of a rotameter, two series-connected midget impingers, a critical orifice, and a pump.

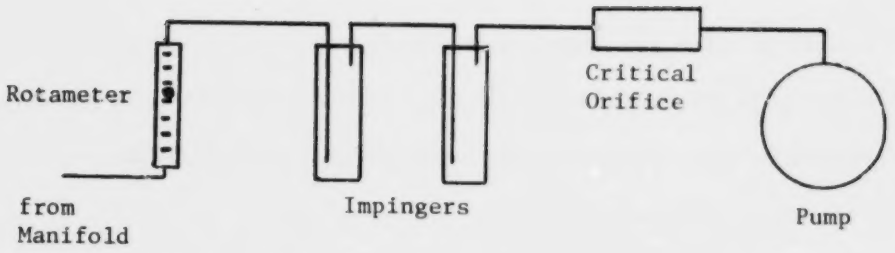

Figure 2. Diagram of Train for Ozone Determination by KI Technique

The rotameter was used only to give a visual indication that the flow rate remained constant. All connectors and inlet tubing were of glass or teflon. Each impinger was labeled so that its position remained the same throughout the studies. The impingers, inlet lines, and manifold were cleaned scrupulously before each calibration run.

D. Sampling Procedure for Determinaing Oxidants by the KI Method

(1) Prepare a solution of 1% neutral KI as prescribed in "Selected Methods Manual." [7]

(2) Prepare a calibration curve using a standard iodine solution--which is standardized using a KIO_3 primary standard and diluted to appropriate volumes with neutral-buffered absorbing solution.

(3) Pipette 10 ml of absorbing reagent into each impinger and assemble the train (Fig. 2). Protect the impinger from exposure to sunlight with suitable wrappings.

(4) Connect the train to the manifold and sample at 1 liter/min for no more than 15 minutes.

(5) Transfer the solution to a 1" absorbance cell and measure the absorbance at 355 mμ in a Spectronic 20. Obtain the

number of μl O_3/ml from a previously prepared calibration working curve where absorbance is plotted against concentration.

(6) Determine the concentration of ozone in pphm using the following formula:

$$\text{pphm } O_3 = \frac{\mu l\ O_3/ml \times ml \text{ solution} \times 10^2}{\text{Volume of gas sampled(liters)}}$$

It is necessary that the working curve be expressed in ozone concentration units (μl/ml) compatible with the volume units of the gas sampled (i. e. both volumes determined at the same barometric pressure).

E. Results of Calibration Experiments

Data from the calibration runs are given in Tables 1 and 2 for Philadelphia; and in Tables 3 and 4 for Denver. During the second calibration at Philadelphia, and during both calibrations at Denver, one run was carried out with no ozone being supplied to the air stream by the UV lamp. This gave a value for the "oxidant background" of the system. Tables 2, 3, and 4 show that the KI solutions were influenced by a background for all the experiments, as were the coulometric instruments. Only in Denver did the CAMP oxidant meter indicate oxidant in the "purified" air stream, whereas the chemiluminescent meter never registered ozone in any blank run. The numbers in parentheses in Tables 2, 3, and 4 are therefore the net values of ozone added by the UV lamp, above the background oxidant in the calibration system. These net values were used in a least-squares analysis of the calibration data in order to determine correction equations for the daily data. Table 5 lists these correction equations derived from the least squares analyses. With these

TABLE 1

CALIBRATION DATA - CAMP STATION - PHILADELPHIA - 21 JUNE 1968

Ozone Concentration (pphm)

NEUTRAL KI(REFERENCE)	COLORIMETRIC	CHEMILUMINESCENT	COULOMETRIC
5.7**	5.1	4.4	4.4
5.1	5.1	4.4	4.3
6.6	7.3	5.8	5.4
6.9	7.3	6.1	5.6
12.0	13.1	11.4	10.2
10.4*	13.5	11.5	10.2
16.5	17.5	15.8	13.8
16.1	17.5	15.8	13.8
21.3**	19.3	17.0	14.7
16.7	19.3	17.0	15.2
17.0*	22.5	20.0	17.6
20.9	23.0	20.0	17.6
25.8*	28.5	25.0	22.5
28.7	28.5	25.0	22.5

* Probable low KI
** Probable high KI

TABLE 2

CALIBRATION DATA - CAMP STATION - PHILADELPHIA - 31 JULY 1968

Ozone Concentration (pphm)

NEUTRAL KI(REFERENCE)		COLORIMETRIC	CHEMILUMINESCENT	COULOMETRIC	
	(-1.8)				(-0.3)
1.83	(0)	0	0	0.3	(0)
3.5	(1.7)	1.5	1.9	2.4	(2.1)
5.5	(3.7)	2.7	3.6	3.6	(3.3)
8.9	(7.1)	8.4	6.3	8.3	(8.0)
10.8	(9.0)	5.1	6.2	6.2	(5.9)
12.1	(10.3)	8.1	9.1	9.1	(8.8)
12.3	(10.5)	7.7	8.7	8.7	(8.4)
14.0	(12.2)	10.0	11.2	10.6	(10.3)
14.9	(13.1)	10.3	11.1	11.0	(10.7)
16.8	(15.0)	12.7	13.6	13.7	(13.4)
17.8	(16.0)	13.9	14.6	14.0	(13.7)
19.0	(17.2)	15.3	16.2	15.2	(14.9)
19.7	(17.9)	17.2	16.4	15.9	(15.6)
20.4	(18.6)	17.2	16.8	15.9	(15.6)
31.4	(29.6)	23.6	24.0	27.0	(26.7)

TABLE 3

CALIBRATION DATA - CAMP STATION - DENVER - 13 AUGUST 1968

Ozone Concentration (pphm)								
NEUTRAL KI (REFERENCE)		COLORIMETRIC		CHEMILUMI-NESCENT	COULOMETRIC A		COULOMETRIC B	
	(-0.7)		(-0.2)			(-0.2)		(-0.4)
0.7	(0)	0.2	(0)	0	0.2	(0)	0.4	(0)
2.4	(1.7)	2.1	(1.9)	1.4	0.6	(0.4)	1.3	(0.9)
3.5	(2.8)	2.7	(2.5)	2.1	1.0	(0.8)	1.7	(1.3)
5.2	(4.4)	3.5	(3.3)	3.0	1.9	(1.7)	3.0	(2.6)
5.7	(5.0)	5.1	(4.9)	4.4	2.8	(2.6)	3.7	(3.3)
7.1	(6.4)	4.8	(4.6)	4.3	2.3	(2.1)	3.9	(3.5)
9.7	(9.0)	7.3	(7.1)	6.7	4.0	(3.8)	6.2	(5.8)
9.8	(9.1)	8.2	(8.0)	7.1	4.3	(4.1)	5.6	(5.2)
13.6	(12.9)	10.0	(9.8)	9.3	5.8	(5.6)	8.1	(7.7)
13.9	(13.2)	10.5	(10.3)	10.0	6.2	(6.0)	9.9	(9.5)
14.4	(13.7)	11.9	(11.7)	10.2	6.0	(5.8)	8.9	(8.5)
17.2	(16.5)	15.3	(15.1)	12.2	8.8	(8.6)	11.2	(10.8)
17.4	(16.7)	13.9	(13.7)	12.4	8.8	(8.6)	12.4	(12.0)
20.9	(20.2)	18.0	(17.8)	15.1	10.3	(10.1)	15.6	(15.2)

TABLE 4

CALIBRATION DATA - CAMP STATION - DENVER - 11 OCTOBER 1968

Ozone Concentration (pphm)								
NEUTRAL KI (REFERENCE)		COLORIMETRIC		CHEMILUMI-NESCENT	COULOMETRIC A		COULOMETRIC B	
	(-0.4)		(-0.4)			(-0.1)		(-0.4)
0.4	(0)	0.4	(0)	0	0.1	(0)	0.4	(0)
5.6	(5.2)	4.3	(3.9)	3.8	3.6	(3.5)	3.2	(2.8)
5.9	(5.5)	5.3	(4.9)	4.2	4.2	(4.1)	2.6	(2.2)
10.2	(9.8)	8.7	(8.3)	7.5	6.4	(6.3)	5.3	(4.9)
13.4	(13.0)	10.9	(10.5)	9.5	8.2	(8.1)	7.0	(6.6)
16.6	(16.2)	13.5	(13.1)	12.1	10.1	(10.0)	9.1	(8.7)
19.0	(18.6)	15.5	(15.1)	14.6	12.1	(12.0)	10.7	(10.3)
21.8	(21.4)	18.2	(17.8)	17.2	14.0	(13.9)	12.8	(12.4)
25.5	(25.1)	20.7	(20.3)	20.4	18.0	(17.9)	15.7	(15.3)
*19.1	(18.7)	*23.0	(22.6)	*16.4	*13.2	(13.1)	*12.3	(11.9)

Coulometric A had a CrO_3 filter in the sampling line

Coulometric B had no CrO_3 filter

*Colorimetric instrument run without CrO_3 filter

TABLE 5

CORRECTION EQUATIONS FROM CALIBRATION EXPERIMENTS
(Values in pphm O_3)

Phil No. 1	$OX(C) = \frac{B - 0.7}{1.02}$	$O_3(C) = \frac{R - 0.3}{0.91}$		$M(C) = \frac{M\,B - 0.5}{0.80}$
Phil No. 2	$OX(C) = \frac{B + 0.3}{0.87}$	$O_3(C) = \frac{R - 0.2}{0.86}$		$M(C) = \frac{M\,B - 0.4}{0.89}$
Denver No. 1	$OX(C) = \frac{B + 0.2}{0.86}$	$O_3(C) = \frac{R}{0.75}$	$M(C) = \frac{M\,A + 0.6}{0.52}$	$M(C) = \frac{M\,B + 0.6}{0.73}$
Denver No. 2	$OX(C) = \frac{B}{0.81}$	$O_3(C) = \frac{R + 0.3}{0.80}$	$M(C) = \frac{M\,A + 0.2}{0.67}$	$M(C) = \frac{M\,B + 0.7}{0.60}$

OX(C) - Corrected oxidant concentration (by colorimetric instrument)

B - Colorimetric meter reading during calibration runs

$O_3(C)$ - Corrected ozone concentration (by chemiluminescent instrument)

R - Chemiluminescent meter reading during calibration runs

M(C) - Corrected oxidant concentration (by coulometric instrument)

M - Coulometric meter reading during calibration runs

M A - with CrO_3 filter

M B - without CrO_3 filter

equations, the "true" concentration of oxidant (expressed as pphm O_3 according to the KI method) can be calculated from any individual instrument reading.

An inspection of Table 5 shows that the chemiluminescent instrument maintained its calibration during both the sampling periods. Neither of the coulometric instruments maintained calibration at either city. (Only the coulometric instrument without CrO_3 filter is reported for Philadelphia. Measurements from the instrument with the filter are so erratic that no confidence can be placed in them.) The total oxidant meter in the Denver CAMP Station maintained its calibration, while the Philadelphia instrument drifted rather badly. However, there is evidence that the sample air flow rate was changed soon after the initial calibration experiment in Philadelphia. There is no record of the exact date on which this change was made, unfortunately. The only manner in which the daily data can be analyzed, then, is to assume that the CAMP Station instrument did not alter its calibration after the flow-rate change was made, and that the correction equation obtained from the last calibration experiment in Philadelphia is valid for the whole sampling period.

Signals from the chemiluminescent ozone meter were recorded on strip charts, and the individual 10-minute ozone concentrations were recorded on daily work sheets. An hourly average was computed from these 10-minute observations. Hourly oxidant averages were also determined from the strip chart recordings of the coulometric instruments. Tentative hourly average values for NO, NO_2, SO_2, and total oxidant from the CAMP Station instruments were also recorded

on the daily work sheets. These work sheets were used to follow the progress of the measurement program,but only the 10-minute ozone and hourly values from the coulometric instrument were used in the data compilations of the next section. All values for NO, NO_2, SO_2, and total oxidant used in the statistical analyses were obtained from the CAMP Station punch tape recorders. These data were validated and supplied by NAPCA.

One other daily observation was recorded--the weather. Ozone and certain other oxidants in polluted atmospheres are formed by photochemical reactions. Weather observations frequently help explain low or high oxidant values. The average UV intensity for a given time period would probably be more useful. The effect of daily weather variations may be minimized in long term studies, but in studies of limited duration they may be important. Accordingly, a simple statement of weather was written on the daily work sheets.

SECTION V

FIELD MEASUREMENT PROGRAM

The sites chosen for this study were the CAMP Stations in Philadelphia and Denver. The regular CAMP Station manifold could not be used, however, since the chemiluminescent meter injects ozone into the sampling manifold during the calibration period of its operation cycle. A separate manifold was set up to serve this instrument in both cities. About 45 cubic feet per minute of outside air was drawn through the manifold. Experiments at the RTI laboratories showed that the ozone remained unchanged at this flow rate. The intake for this special manifold was located above the roof of the CAMP Station at the same level as the regular air intake. In order to be assured that all instruments were sampling the same parcel of air, oxidant instrument sampling probes were attached to the special manifold early in the experimental period in Philadelphia. The instruments sampling from this manifold were not influenced by the ozone injected into the manifold because the chemiluminescent meter was connected to the end outlet (downstream) of the manifold to avoid interference with the other oxidant meters. (Fig. 1)

Other measurements required for this study were made by the standard CAMP Station instruments (NO, NO_2, and SO_2) from the regular manifold. The measurement period in Philadelphia extended from 1 June to 31 July 1968, and that in Denver from 10 August to 11 October 1968.

Through an operating error, the Denver total oxidant meter was attached to the regular manifold from 13 August until 1000 hours on

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3 September. At this latter time, the intake was attached to the temporary manifold. The data have been divided into two periods and analyzed separately. The difference in values from these two periods may have been due to destruction of O_3 in the CAMP Station manifold. This is discussed in Section VII.

SECTION VI

DATA REDUCTION AND ANALYSIS

The complete data tabulations for the study fill more than 125 pages of computer printout. These comprise a computer supplement, EU-395, dated April 1969. The important results from analysis of these data are discussed below.

Unfortunately the CAMP Station instruments yielded no valid data for a large fraction of time. "Valid" total oxidant data require a correction for NO, as explained elsewhere in this report, so that both an oxidant value and an NO value are required for a single data point. If either instrument was malfunctioning, or if either was on a purge cycle, no total oxidant data are available for that period. Validated data from the Philadelphia CAMP Station were obtained for only 46% of the experimental time, and in Denver only 48% of the time. The chemiluminescent instrument operated approximately 97% of the time at both sites.

Although the coulometric oxidant instrument operated satisfactorily mechanically, the oxidant values in Philadelphia, even after correction by the calibration equations (Table 5), differed greatly from the values obtained by the colorimetric instrument. The coulometric instruments responded well during calibration (Tables 1, 2, 3, and 4), but they almost always produced anomalously low data when sampling ambient air. (This point is obvious from an inspection of the data in the computer supplement.) This peculiar behavior is not thought to be due to SO_2, but the reasons for it can only be speculation at the present time.

In Denver, the coulometric instruments responded well to atmospheric oxidants. After correction for the calibration factor, these data compare favorably with the CAMP total oxidant data. However, because the coulometric data from Philadelphia are obviously not representative, no statistical analyses of data from either city were made.

PHILADELPHIA

The sampling period in Philadelphia began 1 June 1968, and ended 31 July 1968, for a total of 61 days. A summary of the data obtained is presented in Table 6. Definitions of the column headings are as follows:

Column 1 - Hour of the day, local standard time.

Column 2 - O_3(R)C is the one-hour averages of all ozone concentrations for the experimental period corrected by the calibration equations given in Table 5. The chemiluminescent instrument makes six (6) observations each hour. If a minimum of 3 observations were recorded for a given one-hour period, an average for that hour was considered valid. The second column under the heading - C - is the number of cases (days) used in deriving the average. Specifically, in Table 6, for the one-hour periods beginning at 0000 hours and extending to 0059 hours, valid data were obtained on each of 61 days. The individual 3 to 6 data points in each 0000 to 0059 hours period were averaged and corrected using the calibration equation (Table 5). The 61 days of data were then averaged and found to be 1.2 pphm.

Column 3 - OX(B)C is the average of all CAMP Station total oxidant concentrations obtained during the one-hour time periods as explained

TABLE 6

DIURNAL MEANS IN PPHM - PHILADELPHIA - JUNE, JULY 1968

TIME	O_3(R)C		OX(B)C		NO		NO_2		SO_2		OX-O_3C		O_3/OX C	
	AVG	C	AVG	C	AVG	C	AVG	C	AVG	C	AVG	C	AVG	C
0000	1.2	61	1.	28	3.	36	5.	57	6.	53	0.	28	.53	23
0100	1.0	61	1.	23	2.	38	5.	57	7.	54	1.	23	.25	21
0200	.9	60	1.	2	2.	37	5.	56	7.	54	0.	2	1.00	2
0300	.9	60	2.	26	2.	38	4.	55	6.	54	1.	26	.27	23
0400	.8	59	1.	27	2.	39	4.	57	6.	52	1.	27	.34	23
0500	.6	59	1.	26	3.	41	4.	57	7.	52	1.	26	.20	22
0600	.6	59	1.	27	5.	42	6.	56	9.	53	1.	27	.18	23
0700	1.3	57	2.	28	5.	42	6.	57	10.	53	1.	28	.55	24
0800	2.7	57	3.	26	4.	41	6.	52	8.	51	0.	26	.94	25
0900	4.2	56	4.	26	3.	36	6.	46	9.	48	0.	26	1.33	25
1000	5.7	57	5.	24	2.	37	6.	46	7.	49	-1.	24	1.66	24
1100	6.6	57	6.	31	1.	42	5.	51	6.	52	-1.	31	1.91	30
1200	6.9	57	5.	35	1.	46	5.	54	6.	54	-1.	35	1.75	33
1300	7.3	59	5.	33	1.	46	5.	54	5.	51	-2.	33	1.91	31
1400	7.0	59	M	0	M	0	M	0	4.	51	M	0	M	0
1500	6.6	59	5.	27	1.	36	5.	49	5.	48	-2.	27	1.70	26
1600	5.7	59	4.	34	2.	43	5.	59	5.	46	-1.	34	1.51	33
1700	5.1	59	4.	30	2.	39	5.	59	5.	48	-1.	30	1.50	29
1800	3.9	59	3.	31	1.	40	5.	59	6.	47	-1.	31	1.39	28
1900	2.5	59	2.	31	2.	39	6.	59	6.	47	1.	31	.57	28
2000	1.7	59	2.	26	3.	36	6.	59	5.	48	1.	26	.30	21
2100	1.4	59	2.	28	3.	37	6.	58	6.	49	1.	28	.39	24
2200	1.1	60	1.	25	4.	33	6.	58	7.	47	1.	25	.17	22
2300	1.0	60	1.	31	3.	40	5.	56	7.	50	1.	31	.31	27

above. The number of days on which valid data were obtained is given in the column C. Data for any one-hour period were considered valid and significant if at least six 5-minute observations were obtained from the NAPCA validation procedure. Since there is an approximate ten minute chemical processing delay in the total oxidant instrument, all data obtained from the NAPCA validation procedure were shifted back ten minutes in time to permit a more realistic comparison with the data from the faster response chemiluminescent instrument. In addition, since NO introduces an error in the total oxidant observation due to its having been oxidized to NO_2 in the CrO_3 scrubber, 11% of the NO concentration recorded at the same time as the total oxidant data is subtracted from the total oxidant data. Specifically, for the one-hour periods beginning at 0010 hours and extending to 0109 hours, valid data (a minimum of 6 observations) were obtained on each of 28 days--and designated as beginning at 0000 hours. The 6 to 12 data points in each hourly period were averaged, corrected by the calibration equation (Table 5), and corrected further by subtracting 11% of the concurrent average NO concentration. The average concentration for the 28 days was then found to be 1 pphm.

Column 4 - NO is the average of all NO concentrations obtained during the one-hour periods. Again, a 10-minute shift of the validated data as obtained from NAPCA was made to compensate for the 10-minute processing delay in the instrument. The column C lists the number of days on which valid data were obtained. Thus, specifically, for the one-hour period beginning at 0010 hours and extending to 0109 hours, valid data (a minimum of 6 observations) were obtained

on 36 days--and designated as beginning at 0000 hours. The individual 6 to 12 points were averaged to give an hourly average NO concentration. The average concentration for the 36 days were averaged and found to be 3 pphm.

Column 5 - NO_2 is the average of all NO_2 observations obtained during one-hour periods. Validation and analysis operations were the same as with NO.

Column 6 - SO_2 is the average of all SO_2 observations obtained during one-hour periods. Validation and analysis operations were the same as with NO.

Column 7 - OX - O_3C is the difference between the average corrected total oxidant concentration and the average corrected ozone concentration. Because only concurrent data were used in these calculations, values found in column 7 are not the simple difference between column 3 and column 2. Specifically, for the time period beginning at 0100 hours and ending at 0159 hours, concurrent valid hourly averages (as explained above, corrected for appropriate calibration, NO, and time delay) for total oxidant and ozone were obtained on only 23 days. The difference of the average of these 23 data, 1 pphm, is tabulated in Column 7 (whereas the difference between Column 3 and Column 2 is 0).

Column 8- O_3/OX C is the ratio of average corrected ozone concentration to average corrected total oxidant concentration for one-hour periods. Because only concurrent data were used in these calculations, values found in this Column 8 are not the simple ratio of Column 2 values

divided by Column 3 values. Also, the number of valid data in Column 8 is sometimes less than the number of valid data in Column 7. This results from the fact that the value for OX is occasionally zero, in which case the ratio O_3/OX is indeterminate; whereas the difference between OX and O_3, although negative, is significant. The values tabulated in Column 8, therefore, are averages of ratios of concurrent 10-minute data points.

SECTION VII

DISCUSSION

PHILADELPHIA

Selected data from Table 6 are plotted in Fig. 3. The overall diurnal behavior depicted by this figure is similar to that found in other studies; i. e. there are NO and NO_2 maxima in early morning and early evening with an ozone or oxidant maximum around 1300 hours. A detailed study of the figure reveals some interesting and very significant points. Most important,(based upon the methods used) the observed values of ozone exceeded the observed values of total oxidant a large percentage of the time during daylight hours. This of course is not physically possible. As will be discussed later, the same observation was made during part of the sampling period in Denver, although quantitatively not to the same extent. Because of the lack of other data, there is little to be gained in speculating on the reasons for these results. It seems unlikely, however, that the instruments malfunctioned during the measurement phases of the experiment in each city, only to operate properly during the calibration phases which followed immediately thereafter.

A second result revealed from a study of Table 6 and Fig. 3, is the co-existence of appreciable concentrations of NO and ozone at certain times of the day. For example, at 0900 hours on the average 3 pphm of NO and 4.2 pphm of ozone are found. Using a rate constant of 10^7 for the reaction of O_3 with NO, the predicted half-life for NO would be of the order of a few seconds. An inspection of the data from individual days shows that the apparent co-existence (from Fig. 6)

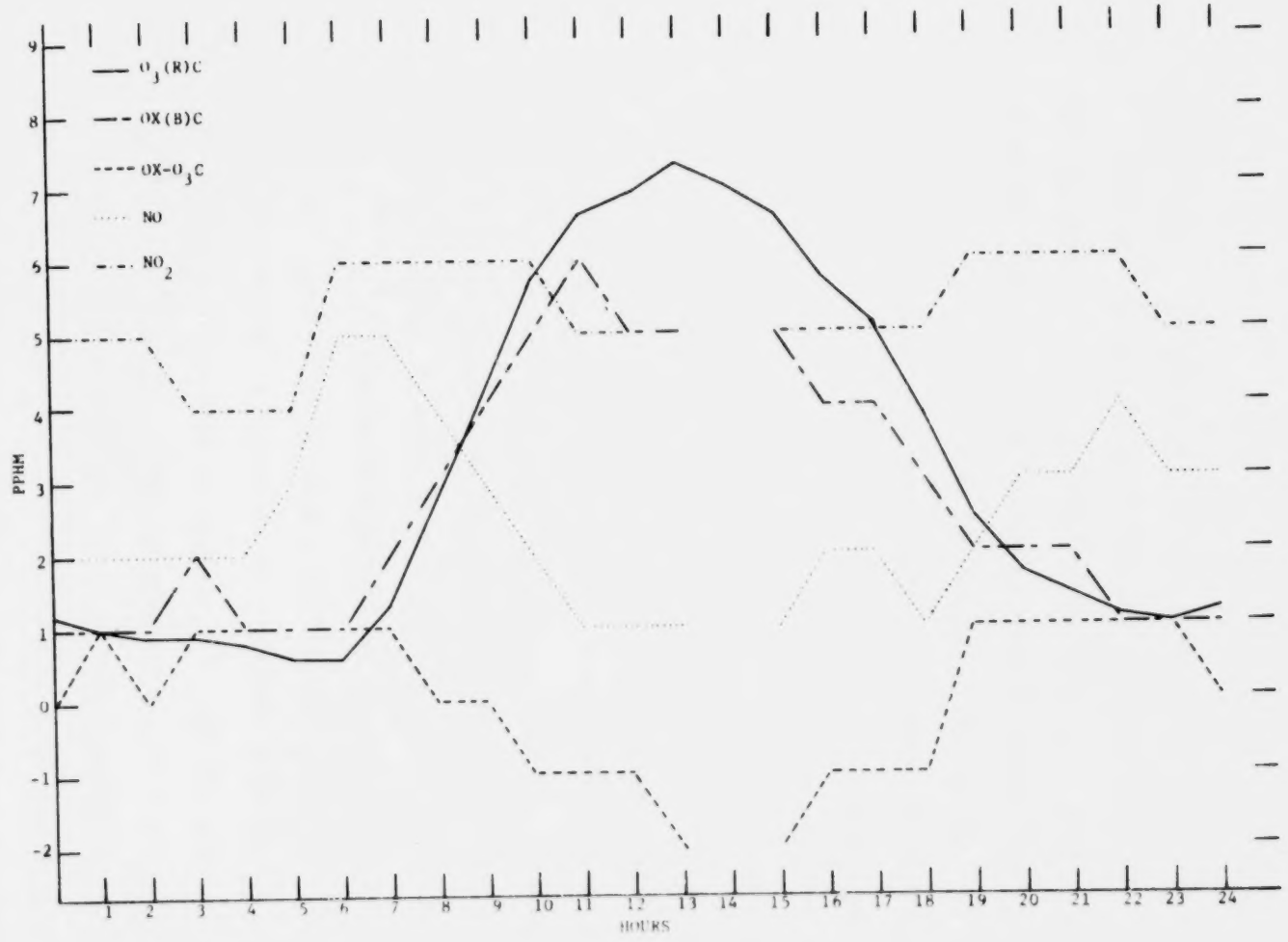

Figure 3. Mean Diurnal Curves - O_3(R)C, OX(B)C, OX-O_3, NO, NO_2 - Philadelphia - June, July 1968

is not due to the way in which the averages were obtained, but rather that the two gases seem to co-exist at these concentrations. One possible explanation is that the two gases do indeed exist simultaneously, the NO being continuously generated in automobile exhaust, and the ozone by photochemical reactions. This explanation requires,however, that the ozone was being generated at an extremely rapid rate.

A third result, apparent from a study of Table 6 and Fig. 3, is the slight increase in ozone concentration between 2200 and 2400 hours. An inspection of data for individual days shows numerous occasions during which ozone (and total oxidant) concentration increased significantly during hours of darkness. For example, Figs. 4, 5, and 6 show hourly average concentrations of various species on 16 June, 25 June, and 14 July respectively in Philadelphia. In the first two curves, the sudden increase in ozone beginning at 2100 hours is unmistakable. Since meteorological measurements were not made at the stations it is not possible to rule out vertical and/or horizontal transport of ozone into the city, but this seems remote. On the other hand, surface sources of nocturnal ozone would be difficult to explain.

Figures 4, 5, and 6 illustrate the other two points discussed above. On June 25 (Fig. 5), for example, the large excess of ozone over total oxidant is very apparent. Also, in Fig. 4, at about 0900, and in Fig. 5 at about 0800, 4 pphm of NO and 4 pphm of ozone were observed.

Table 7 shows a tabulation of the diurnal means of the species measured in this program together with the variance. A study of this table shows a number of cases with large variances about the

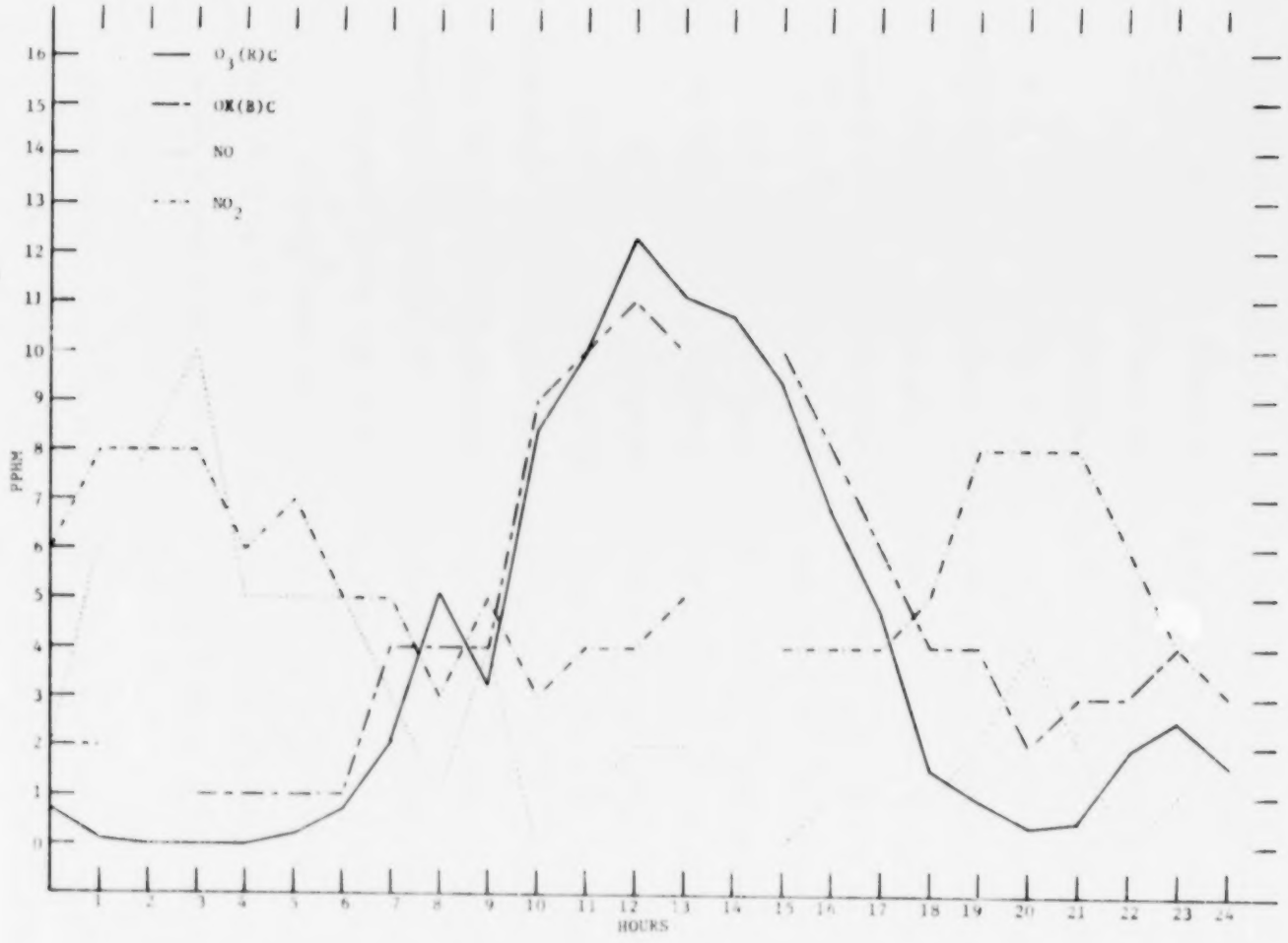

Figure 4. Diurnal Curves - O_3(R)C, OX(B)C, NO, NO_2 - Philadelphia - 16 June 1968

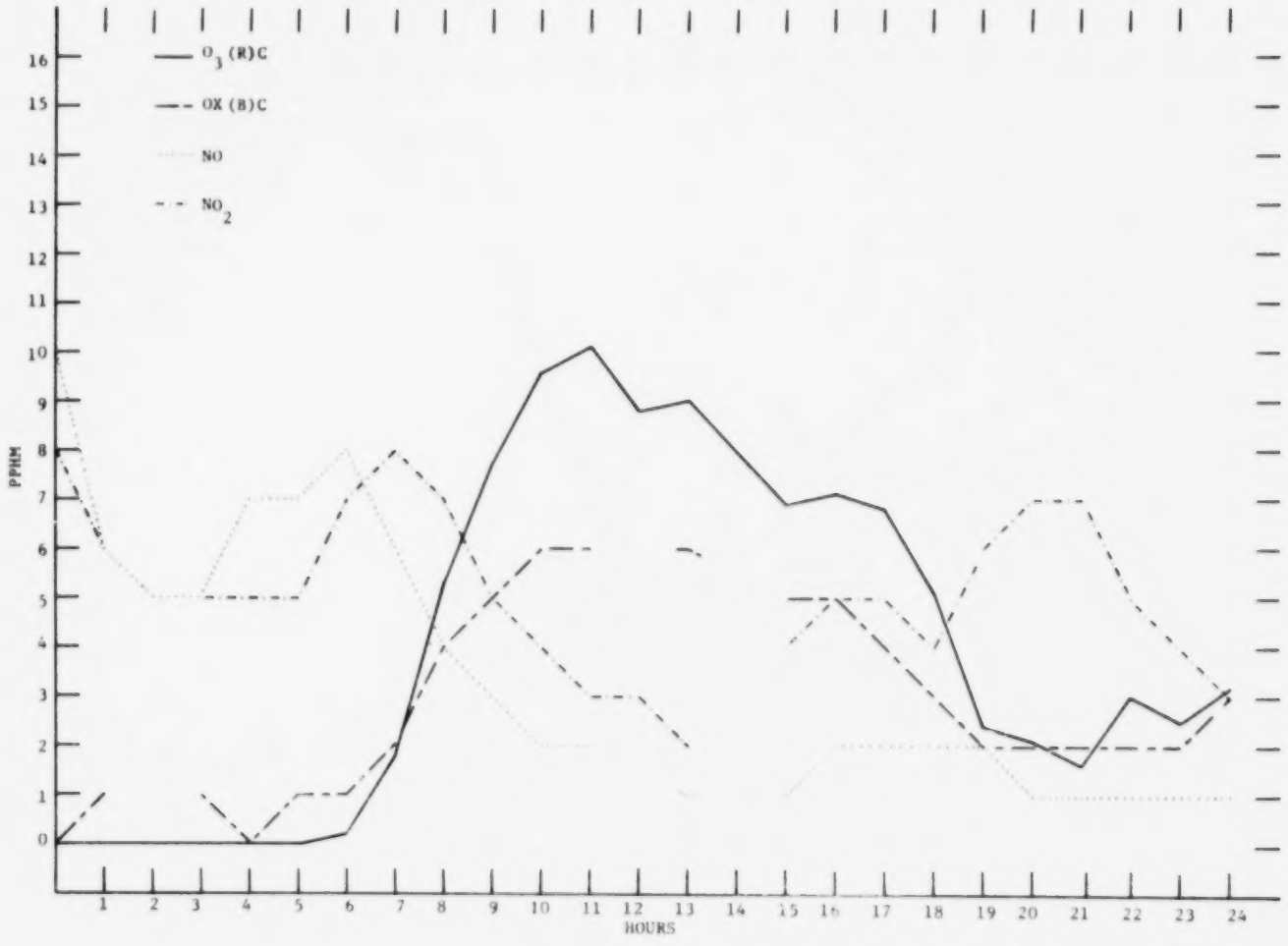

Figure 5. Diurnal Curves - O_3(R)C, OX(B)C, NO, NO_2 - Philadelphia - 25 June 1968

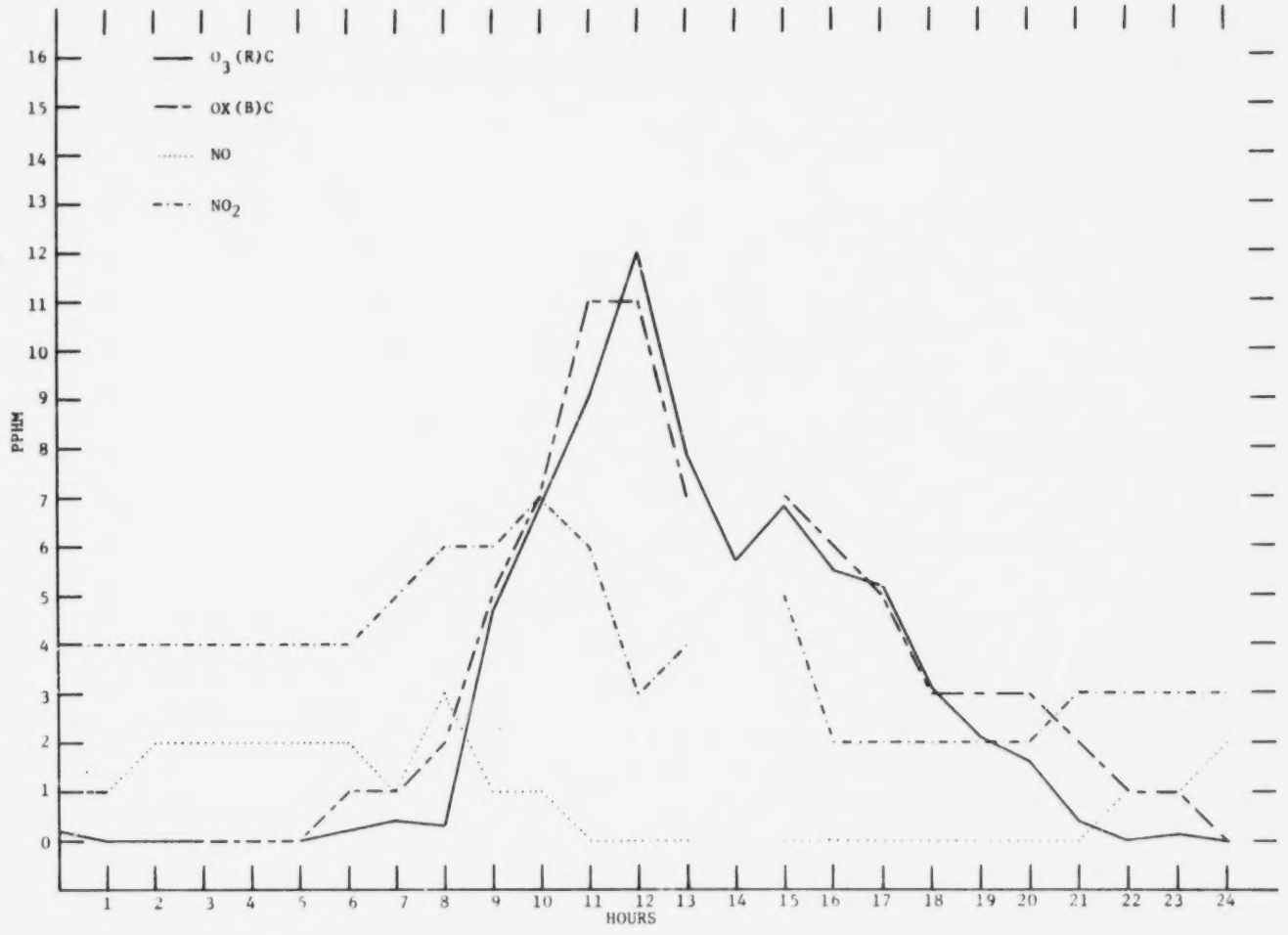

Figure 6. Diurnal Curves - O_3(R)C, OX(B)C, NO, NO_2 - Philadelphia - 14 July 1968

TABLE 7

DIURNAL MEANS IN PPHM AND VARIANCE - PHILADELPHIA - JUNE, JULY 1968

	NO			NO_2			SO_2		
TIME	MEAN	VAR	CAS	MEAN	VAR	CAS	MEAN	VAR	CAS
0000	3.	18.43	36.	5.	5.60	57.	6.	38.13	53.
0100	2.	5.17	38.	5.	5.35	57.	7.	39.85	54.
0200	2.	9.32	37.	5.	7.01	56.	7.	43.78	54.
0300	2.	6.72	38.	4.	5.16	55.	6.	20.97	54.
0400	2.	5.42	39.	4.	3.84	57.	6.	31.07	52.
0500	3.	4.68	41.	4.	3.77	57.	7.	63.30	52.
0600	5.	7.93	42.	6.	6.45	56.	9.	112.25	53.
0700	5.	13.09	42.	6.	10.17	57.	10.	168.27	53.
0800	4.	14.01	41.	6.	10.40	52.	8.	100.40	51.
0900	3.	4.53	36.	6.	9.60	46.	9.	75.80	48.
1000	2.	2.07	37.	6.	7.06	46.	7.	83.54	49.
1100	1.	1.69	42.	5.	5.00	51.	6.	47.79	52.
1200	1.	2.63	46.	5.	5.13	54.	6.	35.18	54.
1300	1.	1.89	46.	5.	3.81	54.	5.	17.00	51.
1400	M	M	0.	M	M	0.	4.	19.16	51.
1500	1.	2.50	36.	5.	2.88	49.	5.	30.26	48.
1600	2.	3.32	43.	5.	5.12	59.	5.	28.98	46.
1700	2.	2.48	39.	5.	4.57	59.	5.	31.19	48.
1800	1.	1.79	40.	5.	7.10	59.	6.	36.34	47.
1900	2.	3.35	39.	6.	9.17	59.	6.	43.78	47.
2000	3.	6.71	36.	6.	8.44	59.	5.	17.91	48.
2100	3.	10.42	37.	6.	7.78	58.	6.	36.28	49.
2200	4.	24.39	33.	6.	7.17	58.	7.	60.74	47.
2300	3.	25.29	40.	5.	6.05	56.	7.	82.28	50.

TABLE 7 (Cont'd)

DIURNAL MEANS IN PPHM AND VARIANCE - PHILADELPHIA - JUNE, JULY 1968

	O_3(R)C			OX(B)C			O_3/OX C		
TIME	MEAN	VAR	CAS	MEAN	VAR	CAS	MEAN	VAR	CAS
0000	1.2	2.45	61.	1.	1.11	28.	.53	1.16	23.
0100	1.0	1.72	61.	1.	.53	23.	.25	.17	21.
0200	.9	1.68	60.	1.	.05	2.	1.00	2.00	2.
0300	.9	1.48	60.	2.	.93	26.	.27	.19	23.
0400	.8	1.49	59.	1.	.79	27.	.34	.21	23.
0500	.6	.99	59.	1.	.45	26.	.20	.16	22.
0600	.6	.70	59.	1.	.69	27.	.18	.11	23.
0700	1.3	1.97	57.	2.	2.32	28.	.55	.44	24.
0800	2.7	3.49	57.	3.	4.44	26.	.94	.95	25.
0900	4.2	10.07	56.	4.	15.64	26.	1.33	1.91	25.
1000	5.7	11.38	57.	5.	12.48	24.	1.67	4.67	24.
1100	6.6	12.18	57.	6.	13.85	31.	1.91	5.47	30.
1200	6.9	14.65	57.	5.	12.55	35.	1.75	5.10	33.
1300	7.3	13.93	59.	5.	12.11	33.	1.91	5.80	31.
1400	7.0	14.46	59.	M	M	0.	M	M	0.
1500	6.6	13.68	59.	5.	9.16	27.	1.70	2.67	26.
1600	5.7	9.67	59.	4.	6.52	34.	1.51	1.62	33.
1700	5.1	8.57	59.	4.	6.06	30.	1.50	2.22	29.
1800	3.9	6.65	59.	3.	3.70	31.	1.30	2.10	28.
1900	2.5	6.83	59.	2.	2.61	31.	.57	.66	28.
2000	1.7	4.14	59.	2.	2.08	26.	.31	.23	21.
2100	1.4	3.30	59.	2.	1.57	28.	.39	.24	24.
2200	1.1	2.41	60.	1.	1.00	25.	.17	.16	22.
2300	1.0	1.65	60.	1.	.96	31.	.31	.36	27.

mean. This reflects the wide dispersion of concentrations of the species in question at a given hour. A tabulation of the daily mean values for the various species will be found in Appendix Table A.

DENVER

The sampling period in Denver began on 10 August 1968 and ended 11 October 1968. As mentioned earlier, the CAMP Station total oxidant instrument sampled air from the regular Station manifold from 10 August until about 1000 hours on 3 September. At that time it was connected to the special ozone manifold for the remainder of the experimental period. Because of the difference in results found during these two periods, the data have been analyzed separately. Table 8 summarizes results for 10 August-2 September and Table 9 summarizes the data for 3 September-11 October. The column headings are the same as those for the Philadelphia data. In Figs. 7 and 8, selected data from these two tables are plotted.

A study and comparison of these tables and figures yields some interesting observations. First, the ozone-total oxidant relationship differed during the two measurement periods. During the period when the total oxidant instrument was sampling from the station manifold, the observed total oxidant instrument was sampling from the station manifold, the observed total oxidant concentration was equal to or less than the observed ozone during most of the daylight hours. When the two instruments were sampling from the special manifold, however, the measured total oxidant exceeded the measured ozone during most

TABLE 8

DIURNAL MEANS IN PPHM - DENVER - AUGUST 10 THROUGH SEPTEMBER 2, 1968

TIME	O_3(R)C		OX(B)C		NO		NO_2		SO_2		OX-O_3C		O_3/OX C	
	AVG	C	AVG	C	AVG	C	AVG	C	AVG	C	AVG	C	AVG	C
0000	1.8	21	2.	4	2.	5	3.	14	1.	14	-1.	4	1.42	3
0100	1.7	21	1.	4	3.	4	3.	15	0	14	0.	4	1.00	3
0200	1.9	21	M	0	2.	5	3.	14	1.	14	M	0	M	0
0300	2.3	21	2.	5	2.	5	2.	14	1.	14	0	5	.83	4
0400	1.9	21	1.	6	3.	6	2.	15	1.	14	0	6	.70	5
0500	1.3	21	1.	6	5.	7	3.	14	1.	13	0	6	1.40	5
0600	1.3	21	2.	4	5.	7	4.	13	1.	13	0	4	1.12	4
0700	2.7	21	4.	4	4.	5	5.	15	1.	14	0	4	1.16	4
0800	4.4	21	5.	5	1.	6	4.	13	1.	13	0	5	1.12	5
0900	6.3	21	6.	5	1.	7	4.	15	1.	14	-1.	5	1.28	5
1000	7.3	21	6.	5	1.	7	3.	15	1.	13	-2.	5	1.35	5
1100	7.3	22	7.	5	1.	7	2.	15	1.	13	-1.	5	1.21	5
1200	7.1	22	6.	7	1.	7	2.	14	1.	14	-2.	7	1.37	7
1300	6.8	22	5.	5	1.	5	3.	12	1.	14	-2.	5	1.35	5
1400	6.7	22	M	0	M	0	2.	2	1.	14	M	0	M	0
1500	5.5	22	4.	6	2.	6	3.	11	1.	13	-2.	6	1.56	6
1600	4.9	21	4.	7	2.	7	3.	12	1.	13	-2.	7	1.44	7
1700	4.9	21	4.	7	1.	7	2.	14	1.	14	-1.	7	1.35	7
1800	3.7	21	3.	7	1.	7	3.	15	1.	14	0	7	1.19	7
1900	2.7	22	3.	6	1.	6	3.	15	1.	14	0	6	1.04	6
2000	1.9	22	2.	7	1.	7	4.	15	1.	14	0	7	1.26	7
2100	1.3	22	1.	7	2.	7	4.	15	1.	14	1.	7	.50	7
2200	1.7	22	2.	6	1.	6	3.	15	1.	15	1.	6	.77	6
2300	1.6	22	2.	6	1.	6	3.	13	1.	15	0	6	.78	6

TABLE 9

DIURNAL MEANS IN PPHM - DENVER - SEPTEMBER 3 THROUGH OCTOBER 11, 1968

TIME	O_3(R)C		OX(B)C		NO		NO_2		SO_2		OX-O_3C		O_3/OX C	
	AVG	C	AVG	C	AVG	C	AVG	C	AVG	C	AVG	C	AVG	C
0000	1.4	39	2.	24	2.	28	3.	31	1.	35	0.	24	.67	21
0100	1.4	39	2.	24	2.	28	3.	31	1.	34	0.	24	.85	21
0200	1.5	39	M	0	1.	27	3.	31	1.	34	M	0	M	0
0300	1.6	39	2.	22	1.	28	2.	31	1.	36	0.	22	.90	21
0400	1.4	39	2.	17	1.	27	3.	31	1.	34	0.	17	.98	16
0500	1.0	39	1.	19	3.	24	3.	31	1.	34	0.	19	.71	16
0600	.9	39	2.	15	7.	19	3.	31	1.	34	1.	15	.60	15
0700	1.5	39	2.	15	8.	21	5.	29	2.	35	1.	15	.79	15
0800	2.9	39	4.	16	5.	25	5.	26	2.	33	1.	16	.72	16
0900	4.6	39	6.	20	3.	24	4.	28	1.	35	1.	20	.75	20
1000	5.8	39	6.	22	2.	26	4.	30	1.	36	0.	22	.95	22
1100	6.4	39	7.	25	2.	30	3.	32	1.	37	1.	25	.91	25
1200	6.3	38	6.	22	2.	28	3.	31	1.	37	0.	22	.98	22
1300	5.9	38	6.	14	2.	29	3.	31	1.	37	0.	14	.95	14
1400	5.9	38	M	0	M	0	M	0	1.	37	M	0	M	0
1500	5.1	38	6.	14	3.	17	4.	27	1.	37	0.	14	.95	14
1600	4.4	38	4.	28	3.	32	4.	31	1.	37	0.	28	1.08	28
1700	3.4	38	3.	29	2.	33	4.	31	1.	37	-1.	29	1.29	29
1800	2.0	38	2.	31	3.	33	4.	31	1.	37	0.	30	.87	28
1900	1.4	38	2.	31	4.	32	4.	31	1.	37	1.	30	.72	29
2000	1.3	38	1.	30	4.	31	4.	31	1.	37	0.	29	.87	28
2100	1.1	38	1.	29	4.	32	4.	31	1.	37	1.	28	.56	24
2200	1.2	38	2.	28	4.	30	3.	31	2.	37	1.	27	.51	21
2300	1.3	38	2.	28	3.	29	3.	31	1.	36	1.	27	.61	26

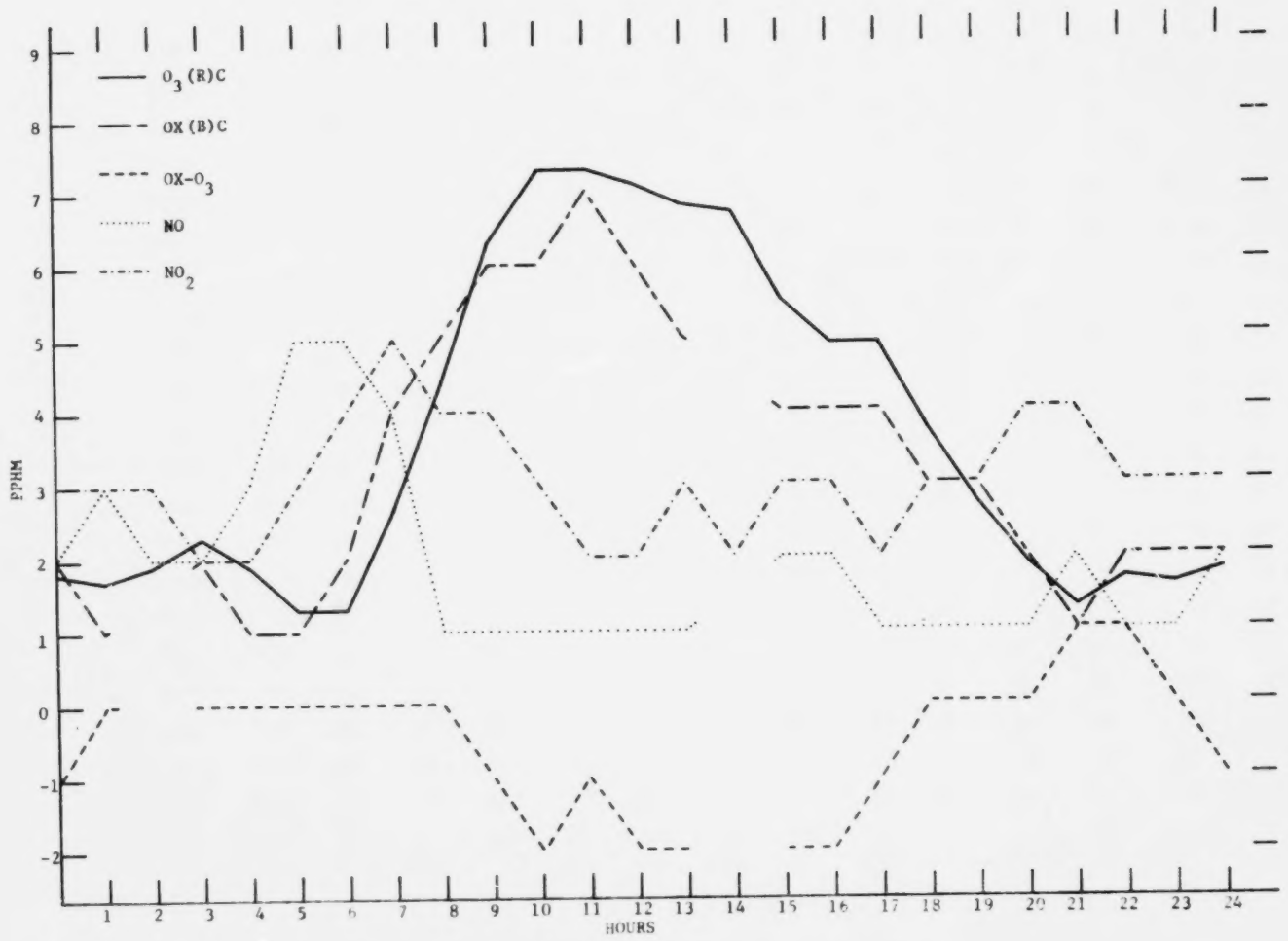

Figure 7. Mean Diurnal Curves - O_3(R)C, OX(B)C, OX-O_3C, NO, NO_2 - Denver - 10 August through 2 September 1968

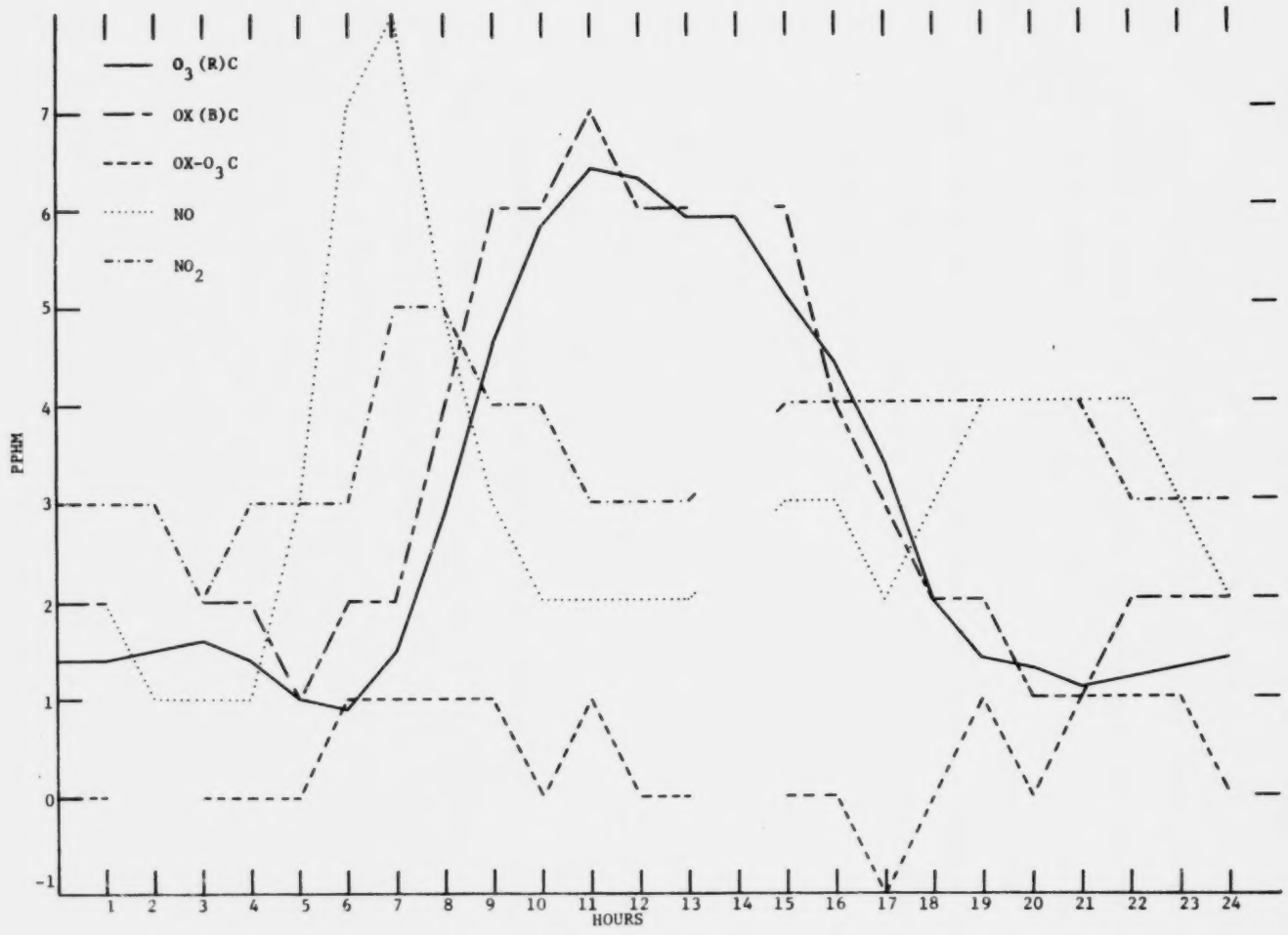

Figure 8. Mean Diurnal Curves - O_3(R)C, OX(B)C, OX-O_3C, NO, NO_2 - Denver - 3 September through 11 October 1968

of these same hours. Whether this is due to a difference in the atmospheric composition during the periods or to partial destruction of oxidants in the station manifold during the first period is not clear. On the other hand, the total oxidant concentrations during the two periods may have been quite similar, but because of the few data from the first period, the deviations may be so great as to obscure similarity.

The assumption that the atmospheric composition may have been different during the two periods is not unreasonable. A further study of the two tables and figures shows that the average ozone concentration during the second period was smaller than during the first. This may be due to a decrease in the daylight hours and consequently a shorter time available for photochemical reactions to produce ozone. Also, the NO maximum occurred at an earlier morning hour during the second period than the first, as well as being greater in magnitude. The average NO concentration during the noon hours was also greater during the second period than the first. All of these observations are consistent with the conclusion that the seasonal factor in atmospheric composition may have some bearing on the differences noted in ozone-total oxidant relationships.

Comparison of Fig. 3 with Figs. 7 and 8 shows among other things that the oxidant maximum in Denver occurred a full two hours earlier than it did in Philadelphia.

Figures 9, 10, and 11 show the hourly concentrations of various species on 18 August, 15 September, and 4 October, respectively, in Denver. As in Philadelphia, there are morning and afternoon

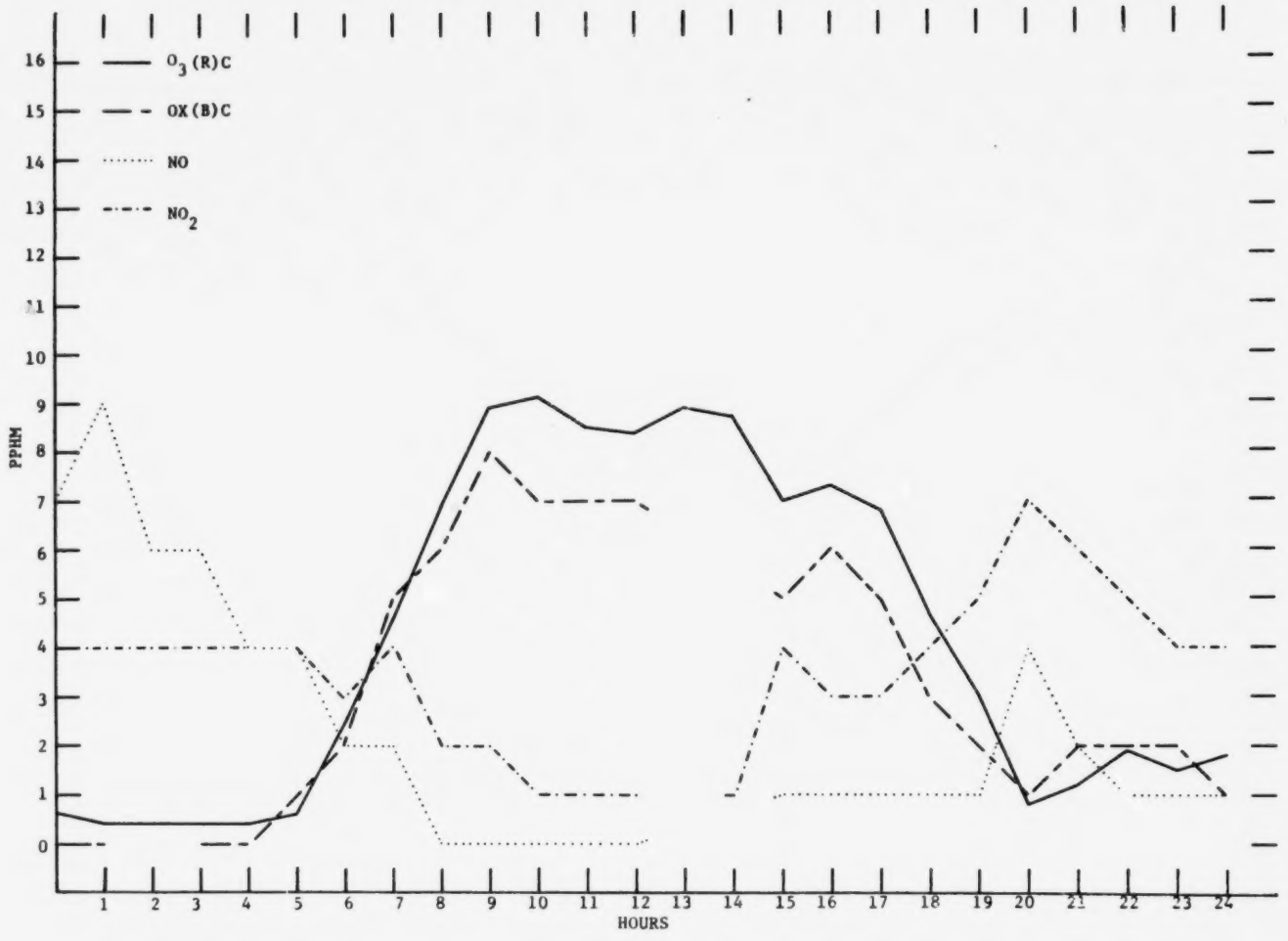

Figure 9. Diurnal Curves - O_3(R)C, OX(B)C, NO, NO_2 - Denver - 18 August 1968

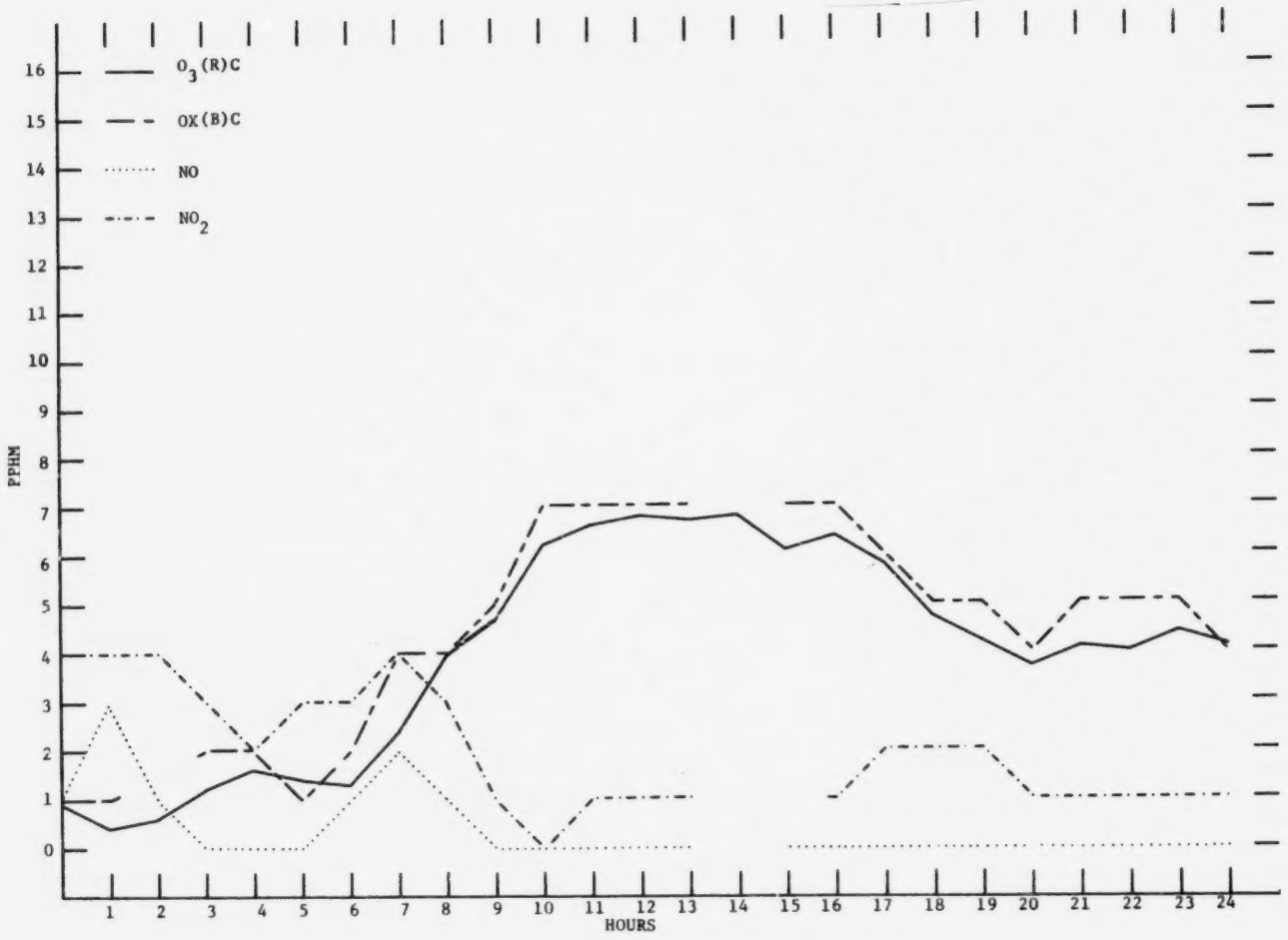

Figure 10. Diurnal Curves - O_3(R)C, OX(B)C, NO, NO_2 - Denver - 15 September 1968

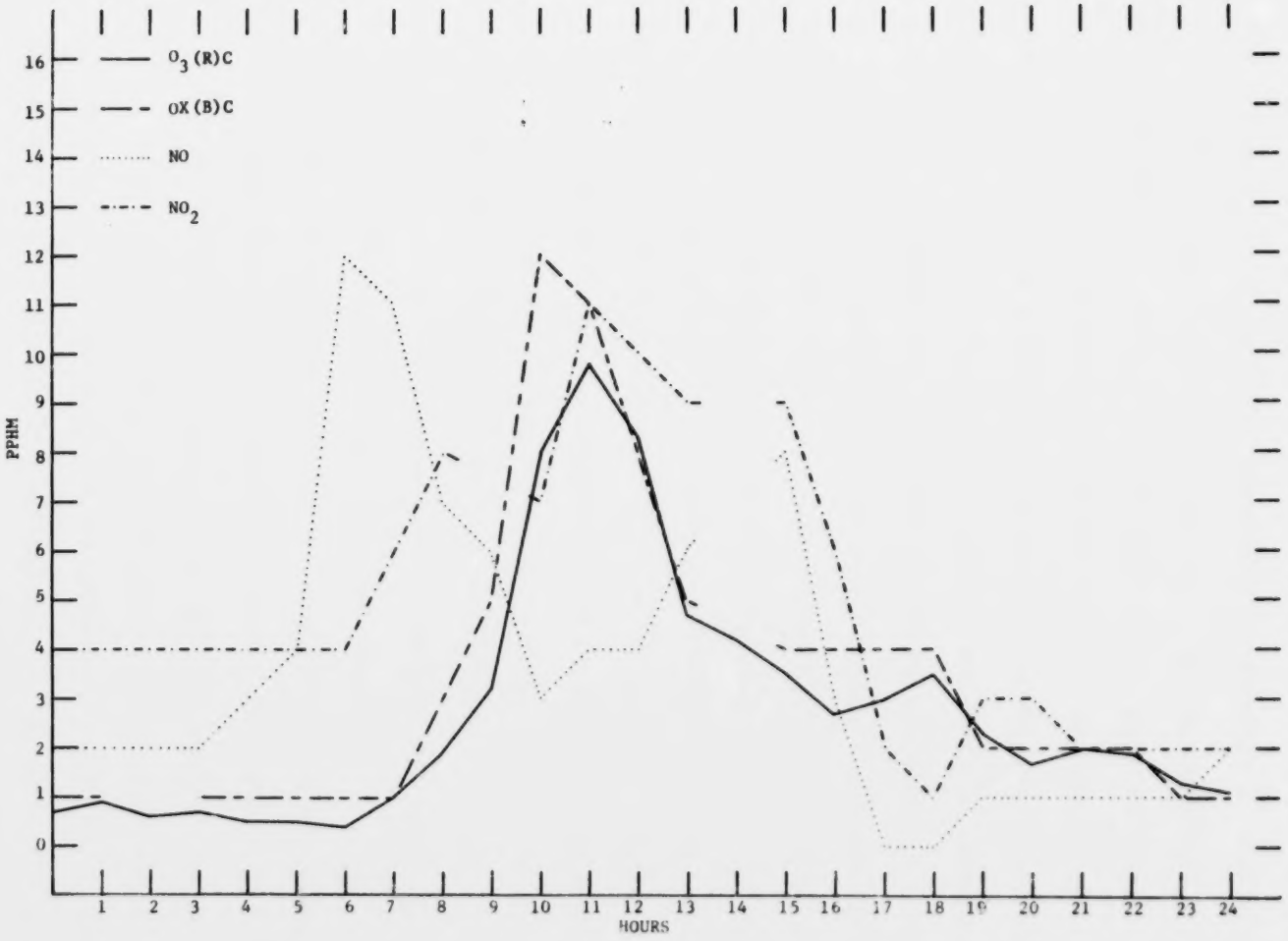

Figure 11. Diurnal Curves - O_3(R)C, OX(B)C, NO, NO_2 - Denver - 4 October 1968

maxima for NO and NO_2 and an oxidant maximum between. In addition, Fig. 9 also shows the unmistakable increase in ozone late at night. The few figures included in this report (Figs. 4, 5, 6, 9, 10, and 11) showing hourly variations of the gases in the two cities, were chosen to indicate the magnitude of ozone or total oxidant on those particular days. An inspection of all of the individual daily curves brings out an important correlation of total oxidant with weather. With each day's observations, a brief description of the average weather was included. As would be expected, on cloudy, rainy days both ozone and total oxidant concentrations were much reduced. Without this simple observation of weather, however, the reasons for low ozone-oxidant values on data sheets may not have been so readily obvious. A further interesting point comes from a study of these ozone-total oxidant relationships on inclement days; i. e. during these days, particularly in Philadelphia, total oxidant concentrations always exceeded ozone concentrations, whereas, as has been discussed earlier, on clear days ozone always exceeded total oxidant concentrations (in Philadelphia). No explanation for this behavior is apparent.

Tables 10 and 11 are included to give a measure of reliability of the Denver data. Variances of the data are given for the two sampling periods. As discussed earlier with the Philadelphia data, variances are large. Again, this reflects the widespread concentration values observed during the experimental period. Also, Tables B and C in the Appendix contain daily mean values of the concentration of the various species. The hourly ratios of average ozone concentration to average total oxidant concentration from which

TABLE 10

DIURNAL MEANS IN PPHM AND VARIANCE - DENVER - AUGUST 10 THROUGH SEPTEMBER 2, 1968

TIME	MEAN	NO VAR	CAS	MEAN	NO_2 VAR	CAS	MEAN	SO_2 VAR	CAS
0000	2.	9.73	5.	3.	2.07	14.	1.	.53	14.
0100	3.	20.68	4.	3.	.84	15.	0.	.25	14.
0200	2.	7.47	5.	3.	.94	14.	1.	.85	14.
0300	2.	7.95	5.	2.	1.57	14.	1.	4.52	14.
0400	3.	11.07	6.	2.	2.19	15.	1.	1.29	14.
0500	5.	14.93	7.	3.	1.10	14.	1.	3.05	13.
0600	5.	30.25	7.	4.	2.00	13.	1.	1.48	13.
0700	4.	6.90	5.	5.	7.01	15.	1.	1.77	14.
0800	1.	.48	6.	4.	4.48	13.	1.	.91	13.
0900	1.	.53	7.	4.	4.22	15.	1.	.67	14.
1000	1.	.21	7.	3.	6.80	15.	1.	1.83	13.
1100	1.	.22	7.	2.	2.83	15.	1.	.40	13.
1200	1.	.23	7.	2.	3.26	14.	1.	.48	14.
1300	1.	.15	5.	3.	3.49	12.	1.	.62	14.
1400	M	M	0.	2.	1.79	2.	1.	.53	14.
1500	2.	1.50	6.	3.	1.73	11.	1.	.37	13.
1600	2.	1.01	7.	3.	1.40	12.	1.	.41	13.
1700	1.	.25	7.	2.	.90	14.	1.	.25	14.
1800	1.	.36	7.	3.	1.52	15.	1.	.57	14.
1900	1.	.29	6.	3.	1.09	15.	1.	2.38	14.
2000	1.	1.57	7.	4.	1.85	15.	1.	2.51	14.
2100	2.	.46	7.	4.	1.68	15.	1.	.88	14.
2200	1.	2.84	6.	3.	1.36	15.	1.	.35	15.
2300	1.	.48	6.	3.	1.13	13.	1.	.35	15.

TABLE 10 (Cont'd)

DIURNAL MEANS IN PPHM AND VARIANCE - DENVER - AUGUST 10 THROUGH SEPTEMBER 2, 1968

	O_3(R)C			OX(B)C			O_3/OX C		
TIME	MEAN	VAR	CAS	MEAN	VAR	CAS	MEAN	VAR	CAS
0000	1.8	1.61	21.	2.	2.70	4.	1.42	.27	3.
0100	1.7	.91	21.	1.	1.12	4.	1.00	0.00	3.
0200	1.9	1.48	21.	M	M	0.	M	M	0.
0300	2.3	1.50	21.	2.	1.40	5.	.83	.33	4.
0400	1.9	1.24	21.	1.	.50	6.	.70	.45	5.
0500	1.3	.74	21.	1.	.12	6.	1.40	.30	5.
0600	1.3	.46	21.	2.	.18	4.	1.12	.06	4.
0700	2.7	1.03	21.	4.	1.70	4.	1.16	.10	4.
0800	4.4	3.17	21.	5.	2.59	5.	1.12	.04	5.
0900	6.3	8.56	21.	6.	1.53	5.	1.28	.08	5.
1000	7.3	6.92	21.	6.	2.65	5.	1.35	.01	5.
1100	7.3	4.20	22.	7.	4.49	5.	1.21	.02	5.
1200	7.1	5.57	22.	6.	2.84	7.	1.37	.07	7.
1300	6.8	7.01	22.	5.	2.11	5.	1.35	.02	5.
1400	6.7	8.10	22.	M	M	0.	M	M	0.
1500	5.5	2.48	22.	4.	.65	6.	1.56	.01	6.
1600	4.9	2.05	21.	4.	1.37	7.	1.44	.03	7.
1700	4.9	1.23	21.	4.	1.05	7.	1.35	.05	7.
1800	3.7	1.21	21.	3.	.70	7.	1.19	.13	7.
1900	2.7	1.75	22.	3.	2.50	6.	1.04	.11	6.
2000	1.9	1.22	22.	2.	.54	7.	1.26	.23	7.
2100	1.3	.67	22.	1.	.19	7.	.50	.17	7.
2200	1.7	.94	22.	2.	1.82	6.	.77	.17	6.
2300	1.6	1.55	22.	2.	1.91	6.	.78	.10	6.

TABLE 11

DIURNAL MEANS IN PPHM AND VARIANCE - DENVER - SEPTEMBER 3 THROUGH OCTOBER 11, 1968

	NO			NO_2			SO_2		
TIME	MEAN	VAR	CAS	MEAN	VAR	CAS	MEAN	VAR	CAS
0000	2.	4.37	28.	3.	1.01	31.	1.	2.18	35.
0100	2.	3.22	28.	3.	.96	31.	1.	2.18	34.
0200	1.	4.44	27.	3.	1.02	31.	1.	2.75	34.
0300	1.	4.79	28.	2.	.95	31.	1.	1.48	36.
0400	1.	.98	27.	3.	.66	31.	1.	2.16	34.
0500	3.	12.05	24.	3.	.88	31.	1.	1.82	34.
0600	7.	33.69	19.	3.	.94	31.	1.	2.31	34.
0700	8.	41.02	21.	5.	3.47	29.	2.	2.39	35.
0800	5.	18.50	25.	5.	5.87	26.	2.	1.23	33.
0900	3.	7.94	24.	4.	5.86	28.	1.	.83	35.
1000	2.	3.06	26.	4.	3.84	30.	1.	1.88	36.
1100	2.	2.69	30.	3.	3.96	32.	1.	3.03	37.
1200	2.	1.77	28.	3.	4.50	31.	1.	1.89	37.
1300	2.	2.04	29.	3.	2.53	31.	1.	3.93	37.
1400	M	M	0.	M	M	0.	1.	.92	37.
1500	3.	5.37	17.	4.	2.57	27.	1.	.77	37.
1600	3.	5.34	32.	4.	1.67	31.	1.	.65	37.
1700	2.	1.73	33.	4.	1.76	31.	1.	.77	37.
1800	3.	9.19	33.	4.	3.93	31.	1.	.67	37.
1900	4.	21.18	32.	4.	2.95	31.	1.	1.06	37.
2000	4.	20.22	31.	4.	1.90	31.	1.	2.01	37.
2100	4.	15.66	32.	4.	1.49	31.	1.	4.82	37.
2200	4.	15.42	30.	3.	1.41	31.	2.	12.44	37.
2300	3.	12.63	29.	3.	1.26	31.	1.	4.80	36.

TABLE 11(Cont'd)

DIURNAL MEANS IN PPHM AND VARIANCE - DENVER - SEPTEMBER 3 THROUGH OCTOBER 11, 1968

	O_3(R)C			OX(B)C			O_3/OX C		
TIME	MEAN	VAR	CAS	MEAN	VAR	CAS	MEAN	VAR	CAS
0000	1.4	1.10	39.	2.	1.60	24.	.67	.18	21.
0100	1.4	1.02	39.	2.	1.73	24.	.85	.31	21.
0200	1.5	1.09	39.	M	M	0.	M	M	0.
0300	1.6	.90	39.	2.	1.20	22.	.90	.18	21.
0400	1.4	.63	39.	2.	1.08	17.	.98	.27	16.
0500	1.0	.73	39.	1.	1.45	19.	.71	.19	16.
0600	.9	.61	39.	2.	.88	15.	.60	.26	15.
0700	1.5	.65	39.	2.	1.11	15.	.79	.20	15.
0800	2.9	2.20	39.	4.	2.14	16.	.72	.05	16.
0900	4.6	6.28	39.	6.	11.19	20.	.75	.04	20.
1000	5.8	6.13	39.	6.	4.25	22.	.95	.15	22.
1100	6.4	6.94	39.	7.	7.40	25.	.91	.03	25.
1200	6.3	4.68	38.	6.	4.34	22.	.98	.02	22.
1300	5.9	3.07	38.	6.	.97	14.	.95	.03	14.
1400	5.9	3.98	38.	M	M	0.	M	M	0.
1500	5.1	3.17	38.	6.	2.41	14.	.95	.03	14.
1600	4.4	2.61	38.	4.	1.88	28.	1.08	.15	28.
1700	3.4	1.36	38.	3.	1.25	29.	1.29	.22	29.
1800	2.0	1.01	38.	2.	1.05	31.	.87	.23	28.
1900	1.4	1.08	38.	2.	.94	31.	.72	.27	29.
2000	1.3	1.06	38.	1.	1.15	30.	.87	.47	28.
2100	1.1	.88	38.	1.	1.20	29.	.56	.18	24.
2200	1.2	1.04	38.	2.	1.69	28.	.51	.25	21.
2300	1.3	1.26	38.	2.	1.05	28.	.61	.58	26.

Tables 6, 8, and 9 are taken are tabulated also in Appendix Tables D, E, and F.

The ozone and total oxidant data can be examined from a different point of view. The ozone oxidant ratios from Tables 6, 8, and 9 are plotted in Fig. 12. The first conclusion to be drawn from this figure is that the ozone total oxidant ratio varies over a wide range: from 0.17 to 1.9. It is not possible, therefore, to arrive at a reliable estimate of the ozone concentration by multiplying an observed total oxidant concentration by a single factor. A second conclusion drawn from Fig. 12, assuming no difference between the CAMP Station instruments, is that the ozone-oxidant ratio varies from city to city and may also vary from season to season in any given city.

Although the quantity of data obtained from the total oxidant instruments during this experiment was only about 48% of the maximum possible, there is no reason to believe that more data would alter greatly either the shape or magnitude of these curves. This assertion is substantiated by an examination of the variance of the ozone and oxidant data in Tables 7, 10, and 11. In Denver, even though only very few concurrent observations of ozone and oxidant were available during the first 21 days, the variance of the data for any given hour is remarkably small, variances of ozone and total oxidant data from Philadelphia are larger, but even so the error in the ratio is seen to be rather small.

If it is true, then, that the ozone-oxidant ratio varies widely from one part of the day to another, the question arises as to how

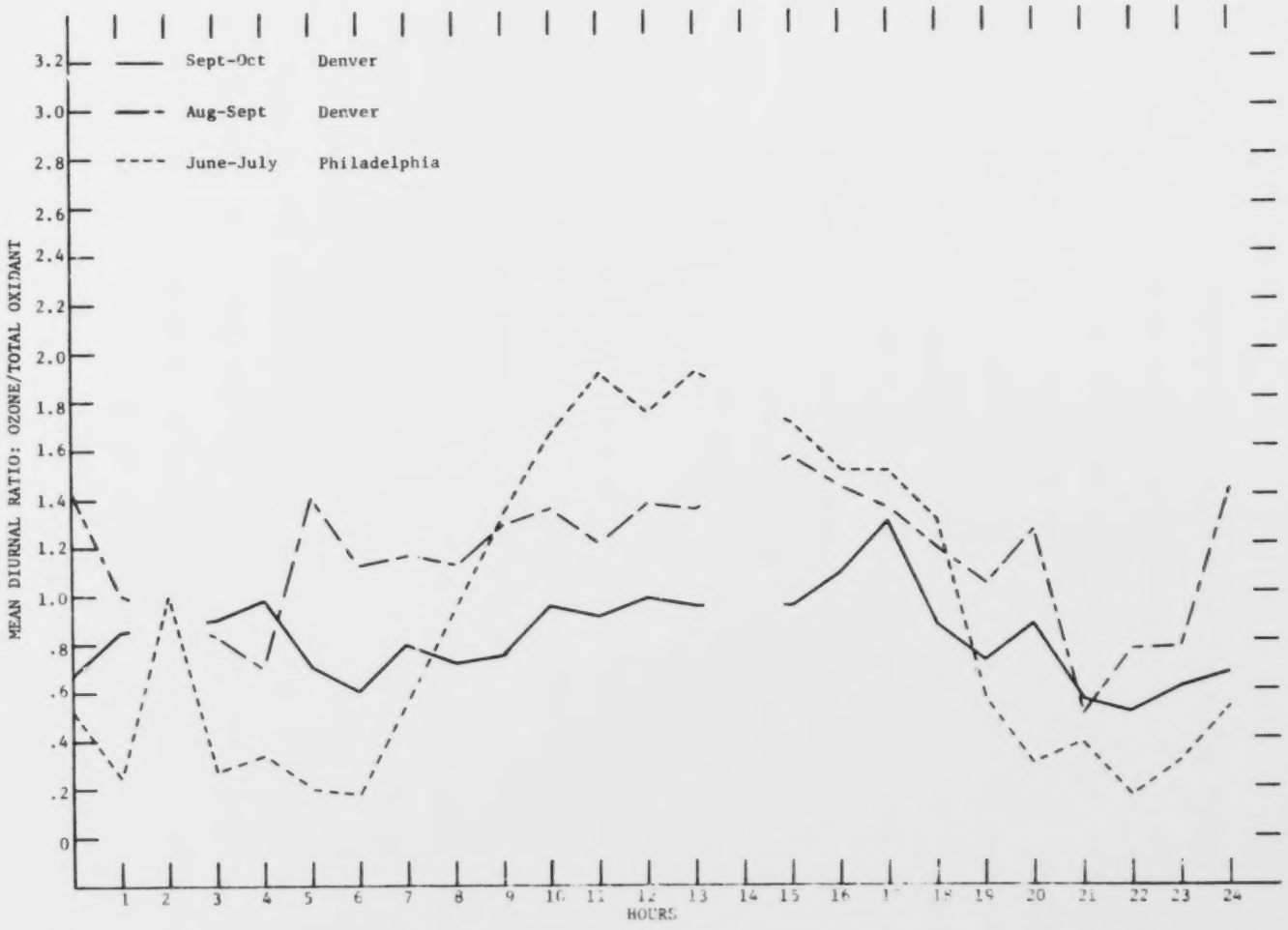

Figure 12. Mean Diurnal O_3/OX Ratios - Philadelphia and Denver

much of, or what part of, the air pollution picture is provided by instruments which measure total oxidants. Certainly, although the two different total oxidant instruments used in this study were maintained according to the best accepted practices, total oxidant results from them were widely different. Furthermore, it is well known that the instruments are not capable of reacting completely, in their customary operational times, with all of the oxidizing agents in polluted air because of slow kinetics. It has been assumed heretofore that a large fraction of observed total oxidant was ozone and that, even though the instruments were not capable of measuring completely all of the oxidants, they were not missing much. This assumption now seems to be unjustified--always assuming, of course, that the chemiluminescent instrument provides a nearly true value for ozone.

In Tables 12, 13, and 14 respectively, are frequency distributions of the ozone-total oxidant ratios (expressed as percentages) for the time periods June 1-July 31 (Philadelphia), August 10-September 2 (Denver), and September 3-October 11 (August). These ratios are calculated from concurrent corrected 10-minute values of ozone and total oxidant by the colorimetric technique. They give an indication of the frequency with which an ozone oxidant ratio occurred as a function of the total oxidant concentration. For example (in Philadelphia) in the total oxidant concentration range of 3-4 pphm, an ozone-total oxidant ratio between 0.61-0.70 (or 61-70%) was observed 56 times during the two month period. That is, 56 pairs of concurrent 10-minute observations

TABLE 12
FREQUENCY DISTRIBUTION
PERCENTAGE MEASURED OZONE VS TOTAL OXIDANT
PHILADELPHIA, PENN. - JUNE 1 THROUGH JULY 31, 1968

$\frac{O_3}{O_x} \times 100$	Total oxidant in pphm											
	0-2	3-4	5-6	7-8	9-10	11-12	13-14	15-16	17-18	19-20	21-22	TOTAL
	Number of Occurrences											
0-10	895	76	3	0	0	1	0	0	0	0	0	975
11-20	67	14	2	1	0	0	0	0	0	0	0	84
21-30	79	28	4	3	1	0	0	0	0	0	0	115
31-40	75	32	6	5	1	1	0	0	0	0	0	120
41-50	56	32	8	2	1	2	1	0	0	1	0	103
51-60	56	44	18	9	4	0	1	0	0	0	0	132
61-70	50	56	19	10	6	2	1	0	0	0	0	144
71-80	30	55	24	13	6	6	2	2	0	0	0	138
81-90	52	43	26	14	11	12	5	0	1	0	0	164
91-100	36	37	33	30	6	12	3	4	3	2	1	167
101-110	31	49	36	32	14	17	0	2	1	0	0	182
111-120	30	49	55	24	11	5	2	2	0	1	0	179
121-130	29	29	49	22	7	3	2	0	0	0	0	141
131-140	17	17	39	21	2	1	1	0	0	0	0	98
141-150	17	19	23	10	0	3	2	1	0	0	0	75
151-160	15	23	34	6	1	1	0	0	0	0	0	80
161-170	16	14	29	2	0	1	0	0	0	0	0	62
171-180	10	11	10	1	0	0	0	0	0	0	0	32
181-190	13	12	9	0	0	0	0	0	0	0	0	34
191-200	5	9	7	0	0	0	0	0	0	0	0	21
>200	268	47	7	0	0	0	0	0	0	0	0	322
TOTAL	1847	696	441	205	71	67	20	11	5	4	1	3368

TABLE 13
FREQUENCY DISTRIBUTION
PERCENTAGE MEASURED OZONE VS TOTAL OXIDANT
DENVER, COLORADO - AUGUST 10 THROUGH SEPTEMBER 2, 1968

0% ($\frac{O_3}{O_x}$ x 100)	Total oxidant in pphm											
	0-2	3-4	5-6	7-8	9-10	11-12	13-14	15-16	17-18	19-20	21-22	TOTAL
	Number of Occurrences											
0-10	0	0	0	0	0	0	0	0	0	0	0	0
11-20	8	4	0	0	0	0	0	0	0	0	0	12
21-30	17	0	1	0	0	0	0	0	0	0	0	18
31-40	14	4	2	1	0	0	0	0	0	0	0	21
41-50	25	1	2	1	0	0	0	0	0	0	0	29
51-60	17	3	1	0	1	0	0	0	0	0	0	22
61-70	18	3	4	3	0	0	0	0	0	0	0	28
71-80	23	3	2	1	1	0	0	0	0	0	0	30
81-90	15	3	5	1	1	0	0	0	0	0	0	25
91-100	26	6	12	5	4	0	0	0	0	0	0	53
101-110	28	12	15	7	1	0	0	0	0	0	0	63
111-120	18	19	19	10	6	0	0	0	0	0	0	72
121-130	13	18	16	9	3	0	0	0	0	0	0	59
131-140	19	8	22	2	4	0	0	0	0	0	0	55
141-150	16	10	25	2	0	0	0	0	0	0	0	53
151-160	12	7	13	0	0	0	0	0	0	0	0	32
161-170	11	7	5	0	0	0	0	0	0	0	0	23
171-180	8	8	3	0	0	0	0	0	0	0	0	19
181-190	10	8	0	0	0	0	0	0	0	0	0	18
191-200	10	3	0	0	0	0	0	0	0	0	0	13
>200	32	7	2	0	0	0	0	0	0	0	0	41
TOTAL	340	134	149	42	21	0	0	0	0	0	0	686

TABLE 14
FREQUENCY DISTRIBUTION
PERCENTAGE MEASURED OZONE VS TOTAL OXIDANT
DENVER, COLORADO - SEPTEMBER 3 THROUGH OCTOBER 11, 1968

% Ozone ($\frac{O_3}{O_x}$ x 100)	Total oxidant in pphm											
	0-2	3-4	5-6	7-8	9-10	11-12	13-14	15-16	17-18	19-20	21-22	TOTAL
	Number of Occurrences											
0-10	0	17	9	1	0	0	0	0	0	0	0	27
11-20	63	52	5	2	0	0	0	0	0	0	0	122
21-30	101	13	5	1	1	0	0	0	0	0	0	121
31-40	114	16	11	4	0	0	0	0	0	0	0	145
41-50	87	20	8	8	1	0	0	0	0	0	0	124
51-60	147	18	26	2	2	0	1	1	0	0	0	197
61-70	87	38	54	7	2	2	0	0	?	2	0	194
71-80	79	48	90	18	11	4	[illegible]	1	1	0	0	255
81-90	69	72	79	26	18	6	0	1	2	0	0	273
91-100	62	74	95	22	6	3	2	0	0	0	0	264
101-110	79	45	97	14	2	2	0	1	0	0	0	240
111-120	66	34	29	4	3	0	0	1	0	0	0	137
121-130	63	17	28	1	2	0	0	0	0	0	0	111
131-140	67	14	6	1	1	0	0	0	0	0	0	89
141-150	37	10	6	1	0	1	0	0	0	0	0	55
151-160	31	10	6	1	0	1	0	0	0	0	0	49
161-170	28	6	3	0	0	1	0	0	0	0	0	38
171-180	20	1	2	1	0	0	0	0	0	0	0	24
181-190	13	4	1	0	2	0	0	0	0	0	0	20
191-200	18	2	1	0	0	0	0	0	0	0	0	21
>200	122	4	1	0	0	0	0	0	0	0	0	127
TOTAL	1353	515	562	114	51	20	6	5	5	2	0	2633

were recorded where the total oxidant concentration was between 3 and 4 pphm and the ozone total oxidant ratio lay between 0.61 and 0.70. There were 696 pairs of concurrent observations during this period where the total oxidant concentration was between 3 and 4 pphm.

Table 15 is a summary of the frequency distribution of the ozone oxidant ratios, giving maxima, minima, and means in the various total oxidant concentration ranges. For example, in Philadelphia, in the total oxidant concentration range of 5-6 pphm, the maximum ozone total oxidant ratio was 2.46 (246%), the minimum ratio was 0, while the mean was 1.17 (117%). There were 441 concurrent ozone total oxidant observations during the period where the total oxidant concentration fell in the 5-6 pphm range.

A value for this ratio of 77.14 (7714%) in the 0-2 pphm total oxidant concentration range, as found in Philadelphia, may seem large but results from the computational method. No rounding of values to digits was performed for these calculations until the ratio of the corrected concencrations had been obtained. Therefore, the ratio of a high value of ozone and a low value of total oxidant, after corrections, can indeed yield a value of 77.14.

TABLE 15
FREQUENCY DISTRIBUTION
PERCENTAGE MEASURED OZONE OF TOTAL OXIDANT
SUMMARY

Station	Total oxidant in pphm 0-2	3-4	5-6	7-8	9-10	11-12	13-14	15-16	17-18	19-20	21-22	Percentage Ozone ($\frac{O_3}{O_x}$ x 100)
	7714	405	246	180	156	161	149	141	107	115	98	Maximum
Philadelphia,	0	0	0	20	22	10	50	77	89	47	98	Minimum
Penn.	150	92	117	104	95	98	97	101	97	87	98	Mean
	1847	696	441	205	71	67	20	11	5	4	1	Cases
	425	263	206	150	138							Maximum
Denver,	15	12	29	40	54							Minimum
Colorado	113	129	123	107	110							Mean
(First Period)	340	134	149	42	21	0	0	0	0	0	0	Cases
	5061	569	227	177	181	166	100	111	87	68		Maximum
Denver,	15	9	7	8	29	62	56	57	65	68		Minimum
Colorado	134	82	89	83	90	95	80	87	75	68		Mean
(Second Period)	1353	515	562	114	51	20	6	5	5	2	0	Cases

SECTION VIII

SUMMARY AND CONCLUSIONS

Ozone and total oxidant were measured simultaneously for two month periods in Philadelphia and Denver. Ozone was measured by the chemiluminescent technique and total oxidant by the colorimetric instruments in the CAMP Stations and a coulometric total oxidant meter. The ozone and oxidant instruments were calibrated from a common standard ozone source at the beginning and end of each experimental period. All instruments were given special attention to assure their proper performance. The experimental period in Philadelphia extended from 1 June to 31 July, 1968, while that in Denver extended from 10 August to 11 October.

The chemiluminescent instrument yielded valid data (3 or more ozone observations in a one-hour period) more than 97% of the time in both sampling sites. Standard CAMP Station instruments yielded valid data (6 or more total oxidant observations together with concurrent NO observations) less than 50% of the time, while the coulometric instrument yielded few interpretable data in Philadelphia.

Except for times of heavy cloud cover or rain, ozone concentration, as measured by the chemiluminescent instrument, usually exceeded total oxidant levels, as measured by the CAMP total oxidant meter, during daylight hours in Philadelphia. The same anomalous results were obtained during the first 21 days in Denver when the total oxidant instrument was sampling from the Station manifold. During the last 40 days

in Denver, when the colorimetric total oxidant instrument was sampling from the special manifold, total oxidant concentrations usually exceeded ozone concentrations.

The ratio of ozone to total oxidant varied in Philadelphia from 0.17 to 1.9, while in Denver it varied from 0.50 to 1.6. It is not possible, therefore, to calculate hourly ozone concentrations from hourly total oxidant measurements with a high degree of reliability. If one is concerned with average dosages over a longer time interval the OX/O_3 ratio may be more useful.

The oxidant maximum occurred 2 hours earlier in Denver than it did in Philadelphia.

On numerous occasions, an increase in ozone and/or total oxidant concentrations was noted during hours of darkness.

On numerous occasions more than 4 pphm of ozone were found to co-exist with 4 pphm of NO.

If oxidant is to be used as an indicator for air quality it appears that a measurement of ozone would be more reliable than total oxidant.

SECTION IX

RECOMMENDATIONS FOR FUTURE WORK

The research reported upon here has provided useful information concerning the statistical relationship between ozone and total oxidant, as well as further insight into their short-period temporal behavior, in an urban environment. At the same time it has emphasized the complexity of the subject of total oxidant with reference to photochemical products in a polluted atmosphere. It has further emphasized the rather serious limitations in the response characteristics of standard measurement techniques in an ambient environment. The inadequacies in measurement techniques, coupled with our lack of knowledge concerning the nature and behavior of total oxidant, makes it extremely difficult to interpret the available data in terms of temporal changes and related physical processes. This is not to say that the operational monitoring programs are not providing useful data, but that there is a limit to our present ability to observe the true nature of the state and behavior of such a complex ambient environmental system.

Although a detailed calibration of instrumentation used in this study was accomplished repeatedly, the need for a thorough comparative evaluation under controlled laboratory conditions is now apparent. The difficulty in accomplishing a study of this nature as an integral part of an operational program is clear.

In order to achieve a better understanding of the total oxidant problem, and to enhance our monitoring capability the following studies are recommended:

(1) Conduct a thorough comparative evaluation of oxidant measurement techniques.

(2) Investigate the interference problem with the colorimetric analytical technique.

(3) Identify and investigate the temporal behavior of the most important constituents in an urban environment which constitute total oxidant (exclusive of O_3 and NO_2).

(4) Identify and investigate the temporal behavior of the most important reducing agents (exclusive of SO_2) in the urban environment.

The above investigations will require much time to carry out properly. In the shorter term, the experimental program described in this report could profitably be repeated in Philadelphia for at least a two-month period--preferably longer. All of the instruments required in the program (chemiluminescent instrument, total oxidant meters, nitrogen oxides meters and SO_2 analyzer) should be under the responsibility of competent technicians throughout the experimental period. The CrO_3 scrubber design should be changed for this study. For the best study, two chemiluminescent ozone meters should be used, one with and one without CrO_3 scrubbers.

Prior to the experimental period, all instruments should be put into top operating condition. In addition, the Station total oxidant meter should be tested in the laboratory for its sensitivity to reducing agents other than SO_2, such as aldehydes and phenols. A CrO_3 scrubber should be used. The chemiluminescent instrument should also be tested for its sensitivity to singlet oxygen which is reported [8] to exist in measurable concentrations in polluted air.

The data gathered during the work discussed in this report should be examined further. First, much total oxidant data had to be rejected because concurrent NO concentration data were missing. Reasonable estimates of these concentrations can be obtained by visual inspection of the individual daily averages. This would yield more total oxidant data for those periods which, under the present method of analysis, have large uncertainties in values because of scarcity of data.

It would be interesting and useful to examine the total oxidant data even without NO concentration corrections. Since NO values seldom were extremely high, the NO correction of only 11% may be relatively unimportant. What would the ozone-total oxidant comparisons look like if NO corrections were not made?

The coulometric total oxidant meter in Philadelphia yielded no useful data. But in Denver, as stated earlier, the instrument produced data which by visual inspection compares favorably with that from the CAMP Station total oxidant meter. These data should be examined further by computer. They should be compared with the CAMP Station total oxidant instrument as well as that from the ozone meter.

Lastly, it would be useful to compare the data obtained during this study with some of that obtained during the previous study, short though it was. It would be especially interesting to compare ozone total oxidant ratios calculated from this study with the same ratios obtained in Denver and Los Angeles in 1967.

SECTION X

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APPENDICES

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TABLE A

DAILY MEAN CONCENTRATIONS

PHILADELPHIA - JUNE, JULY 1968

	June 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
O_3(R)C	2.8	2.7	1.2	1.2	3.1	5.3	4.5	3.0	2.2	1.9	.5	.2	1.1	1.5	6.3
OX(B)C	M	M	2.	M	M	M	M	M	M	M	M	1.	2.	2.	7.
NO	1.	3.	4.	M	M	M	M	M	M	M	M	4.	4.	5.	4.
NO_2	4.	4.	5.	6.	7.	9.	8.	4.	5.	6.	3.	4.	4.	4.	8.
SO_2	3.	6.	12.	M	7.	7.	14.	5.	6.	7.	3.	3.	1.	M	13.
*OX-O_3C	M	M	1.	M	M	M	M	M	M	M	M	1.	1.	1.	1.
*O_3/OXC	M	M	.31	M	M	M	M	M	M	M	M	.07	.49	.39	.48

	June 16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
O_3(R)C	3.9	1.0	3.8	3.9	1.8	M	4.3	3.9	3.8	4.1	2.2	.7	1.2	2.4	4.6
OX(B)C	5.	1.	4.	M	M	M	M	M	4.	3.	1.	0.	0	M	M
NO	3.	5.	2.	1.	2.	4.	M	M	2.	4.	2.	3.	3.	3.	M
NO_2	6.	4.	5.	4.	4.	6.	7.	7.	8.	5.	5.	3.	4.	6.	5.
SO_2	2.	5.	3.	8.	3.	4.	17.	3.	8.	7.	9.	6.	4.	14.	5.
*OX-O_3C	1.	1.	0.	M	M	M	M	M	-1.	-1.	-1.	0.	-1.	M	M
*O_3/OXC	.60	.54	.71	M	M	M	M	M	.88	1.07	M	M	M	M	M

M - missing data

*These ozone-oxidant ratios and differences result from calculations involving concurrent observations of the concentrations of the individual species. These ratios and differences cannot be obtained by using hourly mean values of O_3 and the hourly mean values of OX. See text Part V for complete explanation.

TABLE A (Cont'd)

DAILY MEAN CONCENTRATIONS

PHILADELPHIA - JUNE, JULY 1968

	July 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
O_3(R)C	4.9	3.6	2.2	3.1	5.1	2.7	4.7	4.8	4.2	1.2	2.2	4.0	5.0	3.0	2.9	4.7
OX(B)C	1.	1.	M	M	M	4.	M	6.	4.	1.	M	M	6.	4.	3.	M
NO	2.	3.	3.	M	2.	2.	3.	2.	1.	3.	1.	M	1.	1.	2.	M
NO_2	6.	6.	6.	5.	6.	7.	5.	6.	5.	5.	4.	5.	6.	4.	6.	6.
SO_2	7.	6.	7.	5.	5.	10.	9.	10.	8.	5.	7.	9.	12.	10.	8.	3.
*OX-O_3C	-4.	-3.	M	M	M	1.	M	-1.	0.	1.	M	M	1.	1.	1.	M
*O_3/OXC	5.69	M	M	M	M	.50	M	1.19	1.01	.50	M	M	.59	.54	.43	M

	July 17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
O_3(R)C	4.5	7.0	2.9	2.1	4.0	4.8	6.0	3.1	.9	3.2	3.9	3.4	2.2	3.9	M
OX(B)C	4.	7.	M	M	3.	M	M	M	2.	4.	3.	3.	2.	4.	M
NO	3.	2.	3.	M	1.	1.	2.	5.	3.	2.	0.	1.	5.	5.	1.
NO_2	8.	6.	4.	3.	4.	5.	M	M	6.	4.	3.	3.	5.	5.	5.
SO_2	10.	M	4.	2.	5.	10.	5.	12.	3.	2.	2.	M	0	2.	3.
*OX-O_3C	1.	1.	M	M	-1.	M	M	M	1.	1.	-1.	0.	0	0.	M
*O_3/OXC	.45	.59	M	M	.80	M	M	M	.43	.68	1.24	.90	.95	.70	M

M - missing data

* These ozone-oxidant ratios and differences result from calculations involving concurrent observations of the concentrations of the individual species. These ratios and differences cannot be obtained by using hourly mean values of O_3 and the hourly mean values of OX. See text Part V for complete explanation.

TABLE B

DAILY MEAN CONCENTRATIONS

DENVER - AUGUST 10 THROUGH SEPTEMBER 2, 1968

	Aug. 10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
O_3(R)C	M	6.2	3.9	M	M	3.3	4.4	4.2	4.3	3.7	3.1	4.5	2.9	3.6	4.1
OX(B)C	M	M	M	M	M	M	4.	3.	3.	2.	2.	5.	3.	M	M
NO	M	M	M	M	M	M	1.	1.	2.	2.	3.	1.	2.	M	M
NO_2	6.	M	M	M	M	M	2.	3.	3.	3.	4.	3.	3.	M	M
SO_2	M	M	1.	1.	0	0	M	M	M	0	1.	1.	M	M	M
*OX-O_3C	M	M	M	M	M	M	-1.	-1.	-1.	-1.	-1.	-1.	0	M	M
*O_3/OXC	M	M	M	M	M	M	1.27	1.25	1.15	1.19	.97	1.13	.98	M	M

	25	26	27	28	29	30	31	Sept. 1	2
O_3(R)C	4.7	3.5	3.4	4.1	2.6	3.7	2.9	3.6	3.7
OX(B)C	M	M	M	M	M	M	M	M	M
NO	M	M	M	M	M	M	M	M	M
NO_2	M	4.	3.	3.	3.	4.	3.	2.	1.
SO_2	M	M	1.	1.	1.	2.	1.	2.	1.
*OX-O_3C	M	M	M	M	M	M	M	M	M
*O_3/OXC	M	M	M	M	M	M	M	M	M

M - missing data

*These ozone-oxidant ratios and differences result from calculations involving concurrent observations of the concentrations of the individual species. These ratios and differences cannot be obtained by using hourly mean values of O_3 and the hourly mean values of OX. See text Part V for complete explanation.

TABLE C

DAILY MEAN CONCENTRATIONS

DENVER - SEPTEMBER 3 THROUGH OCTOBER 11, 1968

	Sept. 3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
O_3(R)C	1.7	3.4	3.1	3.0	3.0	3.6	3.5	3.8	3.1	3.3	3.4	3.8	4.0	3.0	2.5
OX(B)C	M	M	M	4.	M	M	M	4.	3.	2.	3.	3.	4.	4.	3.
NO	M	M	M	3.	1.	1.	3.	1.	2.	2.	1.	1.	M	1.	2.
NO_2	M	M	M	M	M	M	M	3.	3.	3.	3.	2.	2.	2.	3.
SO_2	1.	1.	1.	1.	1.	1.	1.	1.	1.	M	1.	M	M	1.	2.
*OX-O_3C	M	M	M	1.	M	M	M	M	M	M	-1.	-1.	1.	M	0
*O_3/OXC	M	M	M	.71	M	M	M	.92	.97	.85	1.23	1.33	.83	1.01	M

	18	19	20	21	22	23	24	25	26	27	28	29	30	Oct. 1	2
O_3(R)C	2.1	2.4	3.1	3.9	3.0	3.2	3.2	2.4	3.4	3.1	2.8	3.4	2.5	2.0	3.0
OX(B)C	M	M	M	M	M	4.	3.	3.	2.	3.	3.	4.	3.	2.	4.
NO	M	1.	3.	M	M	9.	4.	5.	4.	3.	2.	1.	4.	3.	2.
NO_2	3.	3.	4.	3.	4.	6.	5.	4.	5.	4.	3.	3.	4.	3.	2.
SO_2	2.	1.	M	M	0	1.	1.	1.	0	0	0	0	0	1.	1.
*OX-O_3C	M	M	M	M	M	1.	0	0	0	0	1.	1.	1.	1.	1.
*O_3/OXC	M	M	M	M	M	.66	.88	1.01	.74	.80	.77	.83	.58	.68	.84

M - missing data

*These ozone-oxidant ratios and differences result from calculations involving concurrent observations of the concentrations of the individual species. These ratios and differences cannot be obtained by using hourly mean values of O_3 and the hourly mean values of OX. See text Part V for complete explanation.

TABLE C (Cont'd)

DAILY MEAN CONCENTRATIONS

DENVER - SEPTEMBER 3-OCTOBER 11, 1968

	Oct. 3	4	5	6	7	8	9	10	11
O_3(R)C	2.8	2.8	2.5	2.4	2.3	1.9	2.3	1.5	2.9
OX(B)C	3.	3.	3.	3.	3.	2.	3.	2.	M
NO	5.	4.	3.	3.	5.	4.	3.	6.	5.
NO_2	4.	5.	3.	3.	4.	3.	3.	6.	4.
SO_2	2.	3.	2.	3.	3.	2.	4.	4.	2.
*OX-O_3C	1.	1.	0	0	0	0	0	1.	M
*O_3/OXC	.62	.82	.76	.87	.80	.93	.68	.48	M

M - missing data

*These ozone-oxidant ratios and differences result from calculations involving concurrent observations of the concentrations of the individual species. These ratios and differences cannot be obtained by using hourly mean values of O_3 and the hourly mean values of OX. See text Part V for complete explanation.

TABLE D

OZONE-OXIDANT RATIOS, O_3/OX (See Footnote)

PHILADELPHIA - JUNE, JULY 1968

TIME	June 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0000	M	M	0.00	M	M	M	M	M	M	M	M	M	1.00	0.00	0.00
0100	M	M	0.00	M	M	M	M	M	M	M	M	0.00	0.00	0.00	0.00
0200	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
0300	M	M	0.00	M	M	M	M	M	M	M	M	M	1.00	0.00	0.00
0400	M	M	0.00	M	M	M	M	M	M	M	M	0.00	1.00	0.00	0.00
0500	M	M	0.00	M	M	M	M	M	M	M	M	0.00	1.00	0.00	0.00
0600	M	M	0.00	M	M	M	M	M	M	M	M	0.00	0.00	0.00	0.00
0700	M	M	0.00	M	M	M	M	M	M	M	M	0.00	0.00	0.00	M
0800	M	M	0.00	M	M	M	M	M	M	M	M	0.00	M	0.00	.80
0900	M	M	.50	M	M	M	M	M	M	M	M	0.00	M	.50	.91
1000	M	M	M	M	M	M	M	M	M	M	M	.50	M	1.00	1.15
1100	M	1.00	1.00	M	M	M	M	M	M	M	M	M	M	1.00	.93
1200	M	.67	1.25	M	M	M	M	M	M	1.33	M	0.00	.50	.75	1.06
1300	M	1.00	1.00	M	M	M	M	M	M	.67	M	0.00	.67	.80	1.20
1400	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
1500	M	1.00	M	M	M	M	M	M	M	M	M	M	.67	.75	1.09
1600	M	1.00	M	M	M	M	M	M	M	1.00	M	0.00	1.00	1.25	M
1700	M	1.00	M	M	M	M	M	M	M	M	M	.33	.50	1.00	M
1800	M	0.00	M	M	M	M	M	M	M	1.00	M	.50	.50	1.00	M
1900	M	0.00	M	M	M	M	M	M	M	1.00	M	0.00	1.00	.50	M
2000	M	M	M	M	M	M	M	M	M	0.00	M	0.00	0.00	0.00	M
2100	M	0.00	M	M	M	M	M	M	M	1.00	M	0.00	0.00	0.00	M
2200	M	0.00	M	M	M	M	M	M	M	M	M	0.00	0.00	0.00	0.00
2300	M	0.00	M	M	M	M	M	M	M	M	M	0.00	0.00	0.00	0.00

M - missing data

These ozone-oxidant ratios result from calculations involving concurrent observations of the concentrations of the individual species of O_3 by the hourly mean values of OX. These ratios cannot be obtained by dividing hourly mean values See Text Part V for complete explanation.

TABLE D (Cont'd)

OZONE-OXIDANT RATIOS, O_3/OX (See Footnote)

PHILADELPHIA - JUNE, JULY 1968

TIME	June 16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
0000	.50	M	0.00	M	M	M	M	M	M	M	1.00	M	M	0.00	M
0100	0.00	M	0.00	M	M	M	M	M	M	0.00	1.00	1.00	M	M	M
0200	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
0300	0.00	M	0.00	M	M	M	M	M	M	0.00	1.00	M	1.00	M	M
0400	0.00	1.00	0.00	M	M	M	M	M	M	M	1.00	1.00	M	M	M
0500	0.00	1.00	M	M	M	M	M	M	M	0.00	0.00	M	M	M	M
0600	1.00	0.00	M	M	M	M	M	M	M	0.00	M	M	0.00	M	M
0700	.50	M	0.00	M	M	M	M	M	M	1.00	M	M	M	M	M
0800	1.25	1.00	1.00	M	M	M	M	M	.75	1.25	2.00	M	M	M	M
0900	.75	.50	1.00	M	1.00	M	M	M	1.40	1.60	M	M	M	M	M
1000	.89	1.00	M	M	.67	M	M	M	1.43	1.67	M	M	M	M	M
1100	1.00	1.00	1.00	M	.75	M	M	M	1.43	1.67	1.00	M	M	M	8.00
1200	1.09	.75	1.00	M	.75	M	M	M	1.67	M	M	M	M	M	8.00
1300	1.10	1.50	1.00	M	M	M	M	M	1.43	1.50	M	M	M	M	8.00
1400	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
1500	.90	1.00	M	M	.37	M	M	M	1.40	1.40	M	M	M	M	5.00
1600	.87	0.00	.87	M	1.00	M	M	M	1.50	1.40	5.00	M	3.00	M	M
1700	.83	0.00	1.12	M	1.00	M	M	M	1.00	1.75	5.00	M	4.00	M	M
1800	.50	1.00	1.17	M	M	M	M	M	.67	1.67	2.00	M	M	M	8.00
1900	.25	0.00	.71	M	0.00	M	M	M	0.00	1.00	0.00	M	M	M	4.00
2000	0.00	0.00	1.40	M	M	M	M	M	0.00	1.00	M	M	M	M	M
2100	.33	0.00	1.00	M	M	M	M	M	.50	1.00	M	M	M	M	1.00
2200	.67	0.00	M	M	M	M	M	M	0.00	1.50	M	M	0.00	M	0.00
2300	.75	0.00	M	M	0.00	M	M	M	0.00	1.00	M	M	0.00	M	2.00

M - missing data

These ozone-oxidant ratios result from calculations involving concurrent observations of the concentrations of the individual species. These ratios cannot be obtained by dividing hourly mean values of O_3 by the hourly mean values of OX. See Text Part V for complete explanation.

TABLE D (Cont'd)

OZONE-OXIDANT RATIOS, O_3/OX(See Footnote)

PHILADELPHIA - JUNE, JULY 1968

TIME	July 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0000	5.00	M	0.00	M	M	M	M	M	1.33	1.00	0.00	M	M	0.00	M	0.00
0100	M	M	M	M	M	1.00	M	M	M	M	M	M	0.00	0.00	M	M
0200	2.00	M	M	M	M	0.00	M	M	M	M	M	M	M	M	M	M
0300	1.00	M	M	M	M	0.00	M	M	1.00	.50	M	M	0.00	M	0.00	M
0400	M	M	M	M	M	0.00	M	M	1.33	.50	M	M	0.00	M	0.00	M
0500	M	M	M	M	M	0.00	M	M	1.00	0.00	M	M	0.00	M	0.00	M
0600	M	M	M	M	M	0.00	M	M	.50	0.00	M	M	0.00	0.00	M	M
0700	3.00	M	M	M	M	.75	M	M	.50	1.00	M	M	.33	0.00	0.00	M
0800	5.00	M	M	M	M	.86	M	M	.67	.50	M	M	.67	0.00	.67	M
0900	7.00	4.00	M	M	M	.75	M	M	1.00	1.00	M	M	.80	1.00	1.00	M
1000	8.00	9.00	M	M	M	.86	M	M	1.29	0.00	M	.75	.92	1.00	.71	M
1100	9.00	9.00	M	M	M	M	M	1.14	1.33	1.00	M	.82	.92	.82	.62	M
1200	9.00	9.00	M	M	M	1.00	M	1.14	1.17	1.00	.57	1.00	1.22	1.09	.78	M
1300	10.00	9.00	M	M	M	.80	M	1.14	1.14	M	1.12	1.20	M	1.14	.90	M
1400	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
1500	4.00	8.00	M	M	M	.75	M	1.33	1.17	M	1.00	1.25	1.11	1.00	M	M
1600	4.00	6.00	M	M	M	1.00	M	1.33	1.17	2.00	1.40	1.00	.75	.83	.83	M
1700	7.00	3.00	M	M	M	.75	M	1.33	1.20	1.00	1.00	M	1.00	1.00	.75	M
1800	M	3.00	M	M	M	.50	M	1.17	1.00	0.00	1.33	M	M	1.00	1.00	M
1900	M	1.00	M	M	M	.50	M	1.17	1.33	0.00	.33	M	.75	.67	0.00	M
2000	M	M	M	M	M	0.00	M	1.17	1.00	0.00	M	M	M	.67	.50	M
2100	M	M	M	M	M	M	M	1.40	1.00	0.00	M	M	M	0.00	0.00	M
2200	M	M	M	M	M	M	M	1.00	.50	0.00	M	M	M	0.00	0.00	M
2300	M	0.00	M	M	M	0.00	M	1.00	.50	0.00	M	M	1.00	0.00	0.00	M

M - missing data

These ozone-oxidant ratios result from calculations involving concurrent observations of the concentrations of the individual species. These ratios cannot be obtained by dividing hourly mean values of O_3 by the hourly mean values of OX. See Text Part V for complete explanation.

TABLE D (Cont'd)

OZONE-OXIDANT RATIOS, O_3/OX(See Footnote)

PHILADELPHIA - JUNE, JULY 1968

TIME	July 17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
0000	M	0.00	M	0.00	M	0.00	M	M	M	0.00	M	1.00	.50	0.00	.75
0100	.67	0.00	M	M	0.00	0.00	M	M	M	0.00	M	1.00	.50	0.00	M
0200	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
0300	0.00	0.00	M	M	0.00	0.00	M	M	M	.75	0.00	M	0.00	0.00	M
0400	0.00	0.00	M	M	0.00	.50	M	M	M	.75	.67	M	0.00	0.00	M
0500	0.00	0.00	M	M	0.00	0.00	M	M	M	1.00	.33	M	0.00	0.00	M
0600	0.00	0.00	M	M	1.00	.50	M	M	M	.50	.67	0.00	0.00	0.00	M
0700	.67	.25	.75	M	1.00	.75	M	M	M	.50	1.17	0.00	1.00	0.00	M
0800	M	.78	M	M	1.00	1.20	M	M	M	.67	1.50	1.00	.50	.50	M
0900	M	1.00	M	M	1.00	M	M	M	M	1.00	1.25	1.33	1.00	2.00	M
1000	M	1.18	M	M	M	M	M	M	1.00	.80	1.40	1.50	2.50	.75	M
1100	1.10	1.09	1.50	M	M	M	M	M	.67	.86	1.67	1.75	3.00	1.17	M
1200	1.12	M	1.20	M	1.17	M	M	M	1.00	1.00	2.00	1.60	2.00	1.00	M
1300	.90	M	1.67	M	1.50	M	M	M	.75	1.00	2.00	1.60	2.00	1.43	M
1400	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
1500	M	1.18	M	M	1.43	M	M	M	.67	M	2.00	2.00	2.33	1.43	M
1600	1.00	1.11	.75	M	1.67	M	M	M	.67	M	1.67	2.00	1.67	1.00	M
1700	1.00	1.11	M	M	1.50	M	M	M	.33	M	M	1.00	2.00	1.00	M
1800	1.00	1.12	M	M	1.50	M	M	M	.50	M	1.00	1.00	2.00	1.17	M
1900	.25	M	0.00	M	1.25	M	M	M	0.00	M	M	.33	0.00	M	M
2000	0.00	M	0.00	M	.67	M	M	M	0.00	M	M	0.00	0.00	M	M
2100	0.00	M	0.00	M	.50	M	M	M	0.00	M	.50	0.00	0.00	1.20	M
2200	0.00	M	0.00	M	0.00	M	M	M	0.00	M	M	0.00	0.00	M	M
2300	0.00	M	0.00	M	0.00	M	M	M	0.00	M	2.00	0.00	0.00	M	M

M - missing data

These ozone-oxidant ratios result from calculations involving concurrent observations of the concentrations of the individual species. These ratios cannot be obtained by dividing hourly mean values of O_3 by the hourly mean values of OX. See Text Part V for complete explanation.

TABLE E

OZONE-OXIDANT RATIOS, O_3/OX (See Footnote)

DENVER - AUGUST 10 THROUGH SEPTEMBER 2, 1968

TIME	Aug. 10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
0000	M	M	M	M	M	M	M	1.25	M	2.00	M	1.00	M	M	M
0100	M	M	M	M	M	M	1.00	1.00	M	1.00	M	M	M	M	M
0200	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
0300	M	M	M	M	M	M	1.00	1.33	M	1.00	0.00	M	M	M	M
0400	M	M	M	M	M	M	1.50	1.00	M	1.00	0.00	M	0.00	M	M
0500	M	M	M	M	M	M	1.00	2.00	1.00	1.00	M	2.00	M	M	M
0600	M	M	M	M	M	M	M	1.00	1.50	1.00	M	M	1.00	M	M
0700	M	M	M	M	M	M	M	1.50	1.00	1.33	M	M	.80	M	M
0800	M	M	M	M	M	M	M	1.33	1.17	1.25	M	.83	1.00	M	M
0900	M	M	M	M	M	M	1.75	1.20	1.12	M	M	1.00	1.33	M	M
1000	M	M	M	M	M	M	1.50	1.29	1.29	M	M	1.33	1.33	M	M
1100	M	M	M	M	M	M	1.40	1.25	1.14	M	M	1.00	1.25	M	M
1200	M	M	M	M	M	M	1.75	1.50	1.14	1.50	1.50	1.22	1.00	M	M
1300	M	M	M	M	M	M	1.40	M	M	1.17	1.50	1.43	1.25	M	M
1400	M	M	M	M	M	M	M	M	M	M	M	M	M	M	M
1500	M	M	M	M	M	M	1.50	1.67	1.40	1.67	1.50	1.60	M	M	M
1600	M	M	M	M	M	M	1.40	1.67	1.17	1.33	1.50	1.50	1.50	M	M
1700	M	M	M	M	M	M	1.20	1.33	1.40	1.33	1.67	1.50	1.00	M	M
1800	M	M	M	M	M	M	1.00	1.00	1.67	1.50	1.50	1.00	.67	M	M
1900	M	M	M	M	M	M	1.25	1.00	1.50	1.00	M	.50	1.00	M	M
2000	M	M	M	M	M	M	1.33	.50	1.00	1.00	1.50	.50	2.00	M	M
2100	M	M	M	M	M	M	1.00	1.50	.50	1.00	0.00	.50	0.00	M	M
2200	M	M	M	M	M	M	.60	1.00	1.00	1.00	0.00	M	1.00	M	M
2300	M	M	M	M	M	M	1.20	1.00	.50	.50	1.00	M	.50	M	M

M - missing data

These ozone-oxidant ratios result from calculations involving concurrent observations of the concentrations of the individual species. These ratios cannot be obtained by dividing hourly mean values of O_3 by the hourly mean values of OX. See Text Part V for complete explanation.

TABLE E (Cont'd)

OZONE-OXIDANT RATIOS, O_3/OX(See Footnote)

DENVER - AUGUST 10 THROUGH SEPTEMBER 2, 1968

TIME	Aug. 25	26	27	28	29	30	31	Sept 1	2
0000	M	M	M	M	M	M	M	M	M
0100	M	M	M	M	M	M	M	M	M
0200	M	M	M	M	M	M	M	M	M
0300	M	M	M	M	M	M	M	M	M
0400	M	M	M	M	M	M	M	M	M
0500	M	M	M	M	M	M	M	M	M
0600	M	M	M	M	M	M	M	M	M
0700	M	M	M	M	M	M	M	M	M
0800	M	M	M	M	M	M	M	M	M
0900	M	M	M	M	M	M	M	M	M
1000	M	M	M	M	M	M	M	M	M
1100	M	M	M	M	M	M	M	M	M
1200	M	M	M	M	M	M	M	M	M
1300	M	M	M	M	M	M	M	M	M
1400	M	M	M	M	M	M	M	M	M
1500	M	M	M	M	M	M	M	M	M
1600	M	M	M	M	M	M	M	M	M
1700	M	M	M	M	M	M	M	M	M
1800	M	M	M	M	M	M	M	M	M
1900	M	M	M	M	M	M	M	M	M
2000	M	M	M	M	M	M	M	M	M
2100	M	M	M	M	M	M	M	M	M
2200	M	M	M	M	M	M	M	M	M
2300	M	M	M	M	M	M	M	M	M

M - missing data

These ozone-oxidant ratios result from calculations involving concurrent observations of the concentrations of the individual species. These ratios cannot be obtained by dividing hourly mean values of O_3 by the hourly mean values of OX. See Text Part V for complete explanation.

TABLE F

OZONE-OXIDANT RATIOS, O_3/OX (See Footnote)

DENVER - SEPTEMBER 3 THROUGH OCTOBER 11, 1968

TIME	Sept. 3	4	5	6	7	8	9	10	11	12	13	14	15	16
0000	M	M	M	M	M	M	M	.50	.50	1.00	1.00	M	1.00	1.00
0100	M	M	M	.67	M	M	M	1.00	1.00	.67	1.00	1.00	0.00	.80
0200	M	M	M	M	M	M	M	M	M	M	M	M	M	M
0300	M	M	M	1.00	M	M	M	1.00	1.00	1.00	2.00	1.33	.50	1.00
0400	M	M	M	1.00	M	M	M	M	1.00	2.00	1.00	1.00	1.00	1.00
0500	M	M	M	M	M	M	M	M	1.00	M	1.00	1.00	1.00	.50
0600	M	M	M	M	M	M	M	M	0.00	M	M	1,50	.50	1.00
0700	M	M	M	M	M	M	M	M	.50	M	.50	M	.50	.75
0800	M	M	M	M	M	M	M	M	.33	M	.57	M	1.00	.80
0900	M	M	M	.50	M	M	M	M	1.00	M	1.08	M	1.00	.80
1000	M	M	M	1.00	M	M	M	M	1.00	M	1.33	M	.86	1.00
1100	M	M	M	M	M	.89	1.00	.93	1.00	M	1.40	M	1.00	1.00
1200	M	M	M	1.00	M	.90	1.12	.91	1.40	M	M	1.40	1.00	1.00
1300	M	M	M	.87	M	1.00	M	M	M	M	M	1.00	1.00	M
1400	M	M	M	M	M	M	M	M	M	M	M	M	M	M
1500	M	M	M	1.11	M	.86	M	M	M	M	M	1.14	.86	M
1600	M	M	M	1.17	M	.86	1.00	1.00	1.00	1.00	1.33	1.33	.86	M
1700	M	M	M	1.00	M	1.20	1.00	1.00	1.00	1.50	2.00	2.00	1.00	1.00
1800	M	M	M	1.00	M	1.00	1.00	1.00	.67	1.00	2.00	2.00	1.00	1.00
1900	M	M	M	0.00	M	.50	.50	0.00	1.00	1.00	1.00	1.00	.80	1.50
2000	M	M	M	1.00	M	1.00	1.00	1.00	3.00	0.00	M	1.00	1.00	2.00
2100	M	M	M	0.00	M	M	.50	1.00	1.00	1.00	M	.50	.80	M
2200	M	M	M	0.00	M	M	0.00	.67	1.00	0.00	M	1.00	.80	M
2300	M	M	M	0.00	M	M	0.00	2.00	1.00	0.00	M	3.00	.80	M

M - missing data

These ozone-oxidant ratios result from calculations involving concurrent observations of the concentrations of the individual species. These ratios cannot be obtained by dividing hourly mean values of O_3 by the hourly mean values of OX. See Text Part V for complete explanation.

TABLE F (Cont'd)

OZONE-OXIDANT RATIOS, O_3/OX(See Footnote)

DENVER - SEPTEMBER 3 THROUGH OCTOBER 11, 1968

TIME	Sept. 17	18	19	20	21	22	23	24	25	26	27	28	29	30
0000	M	M	M	M	M	M	M	0.00	.67	0.00	1.00	0.00	.75	.67
0100	2.00	M	M	M	M	M	M	M	1.50	0.00	1.00	0.00	.75	2.00
0200	M	M	M	M	M	M	M	M	M	M	M	M	M	M
0300	M	M	M	M	M	M	M	M	M	1.00	1.00	1.00	.80	0.00
0400	M	M	M	M	M	M	M	M	M	M	M	1.00	1.00	1.00
0500	M	M	M	M	M	M	M	M	M	M	M	1.00	.80	0.00
0600	M	M	M	M	M	M	M	M	M	0.00	M	1.00	1.00	.50
0700	M	M	M	M	M	M	M	.50	M	1.00	M	M	1.00	.50
0800	.75	M	M	M	M	M	.40	M	1.00	M	.40	M	.75	1.00
0900	.80	M	M	M	M	M	.47	M	.50	M	.71	M	1.00	.33
1000	.80	M	M	M	M	M	2.50	.60	1.00	M	1.00	.75	.80	.80
1100	.83	M	1.00	M	M	M	.80	1.00	1.00	M	.87	.80	1.00	1.00
1200	M	M	1.00	M	M	M	.86	.87	1.00	M	.89	.90	M	M
1300	M	M	M	M	M	M	M	M	1.00	1.33	M	M	M	1.00
1400	M	M	M	M	M	M	M	M	M	M	M	M	M	M
1500	M	M	M	M	M	M	M	M	1.00	.83	M	M	.71	1.00
1600	1.00	M	1.25	M	M	M	1.20	1.17	2.50	1.00	1.50	M	1.00	1.00
1700	1.33	M	1.50	M	M	M	1.67	1.25	3.00	1.33	1.67	M	.75	1.33
1800	1.00	M	1.00	M	M	M	M	1.00	M	.50	0.00	1.00	1.00	0.00
1900	1.00	M	2.00	M	M	M	0.00	1.00	M	.50	0.00	.60	.50	0.00
2000	1.00	M	1.00	M	M	M	0.00	1.00	0.00	1.00	1.00	.80	1.00	0.00
2100	M	M	M	M	M	M	0.00	.50	M	.50	1.00	.75	.50	0.00
2200	M	M	0.00	M	M	M	0.00	1.50	0.00	.67	M	1.00	.50	0.00
2300	0.00	M	1.00	M	M	M	0.00	1.00	0.00	1.50	0.00	1.00	1.00	0.00

M - missing data

These ozone-oxidant ratios result from calculations involving concurrent observations of the concentrations of the individual species. These ratios cannot be obtained by dividing hourly mean values of O_3 by the hourly mean values of OX. See Text Part V for complete explanation.

TABLE F (Cont'd)

OZONE-OXIDANT RATIOS, O_3/OX (See Footnote)

DENVER - SEPTEMBER 3 THROUGH OCTOBER 11, 1968

TIME	Oct. 1	2	3	4	5	6	7	8	9	10	11
0000	1.00	0.00	1.00	1.00	1.00	M	M	1.00	M	0.00	1.00
0100	0.00	M	.75	1.00	M	M	M	.75	M	1.00	1.00
0200	M	M	M	M	M	M	M	M	M	M	M
0300	.50	M	.67	1.00	1.00	1.00	0.00	1.00	M	M	1.00
0400	1.00	M	M	0.00	.67	2.00	M	1.00	M	0.00	M
0500	1.00	M	M	1.00	1.00	1.00	0.00	1.00	0.00	0.00	M
0600	0.00	M	M	0.00	1.00	1.00	M	1.00	.50	0.00	M
0700	.67	M	M	1.00	1.00	1.00	0.00	2.00	M	M	1.00
0800	.75	M	M	.67	.75	.75	.60	1.00	M	M	M
0900	.75	.80	.67	.60	.80	.67	.80	1.00	.75	M	M
1000	.60	.83	.80	.67	.80	.86	M	1.00	.60	M	1.20
1100	M	.83	.67	.91	.83	1.00	.80	1.00	.67	.40	M
1200	M	.83	M	1.00	.83	1.00	1.00	1.00	.83	1.00	M
1300	M	.83	M	1.00	.83	1.00	1.00	M	.83	.60	M
1400	M	M	M	M	M	M	M	M	M	M	M
1500	.75	M	M	.75	1.00	1.00	M	M	1.00	1.33	M
1600	1.00	1.00	.67	.75	1.00	1.25	1.00	0.00	1.00	1.33	M
1700	1.00	1.00	1.50	.75	1.50	1.00	1.00	1.00	1.00	1.00	M
1800	.67	1.00	1.00	1.00	1.00	0.00	1.00	1.00	.50	0.00	M
1900	1.50	1.00	1.00	1.00	1.00	0.00	1.00	1.00	.50	0.00	M
2000	1.00	1.00	0.00	1.00	0.00	M	2.00	.50	0.00	1.00	M
2100	0.00	1.00	0.00	1.00	0.00	1.00	1.00	.50	1.00	0.00	M
2200	M	1.00	0.00	1.00	0.00	1.00	.67	M	M	M	M
2300	0.00	.67	0.00	1.00	0.00	0.00	1.00	M	1.00	0.00	M

M - missing data

These ozone-oxidant ratios result from calculations involving concurrent observations of the concentrations of the individual species. These ratios cannot be obtained by dividing hourly mean values of O_3 by the hourly mean values of OX. See Text Part V for complete explanation.